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North American Rockwell

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FINAL REPORT

STUDY OF THE PRODUCTION OF UNIQUE NEW GLASSES

Prepared for:

National Aeronautics and Space Administration
George C. Marshall Space Flight Center
Marshall Space Flight Center, Alabama

Prepared by:

Contract NAS8-28014
Space Division, North American Rockwell Corporation
Downey, California

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13 June 1972

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Final Report R.A.
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FOREWORD

This report presents the results of a six-months study performed by the North American Rockwell (NR) Corporation for the NASA Marshall Space Flight Center under Contract NAS8-28014.

The study was managed by the NR-Space Division, who also performed the study on processes and equipment and prepared the future work plan. Glass experiments were performed by the NR-Science Center. The Optical Group of the Perkin-Elmer Corporation performed an applications survey under sub-contract to the NR-Space Division.

The assistance of two consultants is acknowledged. Dr. Milton Blander of Argonne National Laboratories (formerly of the NR Science Center) provided consultation assistance in connection with the experimental work on laser melting. Dr. J. D. McKenzie of U.C.L.A. offered helpful suggestion on the planning of the program.

Special acknowledgement is hereby given to Dr. Emil Deeg and Dr. Harold Osterberg, both of the American Optical Corporation. Dr. Deeg kindly assisted in the preparation of the section dealing with conventional glasses. Dr. Osterberg offered many valuable suggestions on optical properties measurements of small spherules and also assisted with some of the experimental determinations.



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Ralph A. Happe, Principal Investigator

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TABLE OF CONTENTS

	<u>PAGE</u>
INTRODUCTION AND SUMMARY	1
POTENTIAL APPLICATIONS FOR UNIQUE SPACE PRODUCED GLASSES	5
GLASS EXPERIMENTS	7
CHOICE OF SYSTEMS	7
EXPERIMENTAL	9
RESULTS AND DISCUSSION	16
PROCESS AND EQUIPMENT STUDY	29
BASIC MELTING METHODS	31
Induction	31
Laser	43
Resistance Furnace	46
Electron Beam	46
Solar	46
Chemical	47
Arc	48
CHAMBERS	48
PREHEATING	50
POSITION CONTROL	50
COOLING	51
CONVENTIONAL GLASSES IN ZERO G	57
FUTURE WORK PLAN	60
MASTER PLAN	60
WORK RECOMMENDED DURING NASA FY 73	66
APPENDIX I - APPLICATIONS FOR NEW GLASS TYPES PRODUCED BY ZERO GRAVITY (ATTACHED) FABRICATION TECHNIQUES - Perkin-Elmer Engineering Report 10952	AI-1
APPENDIX II - INDUCTION MELTING POWER REQUIREMENT CALCULATIONS	AII-1

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LIST OF FIGURES

- | | |
|------------|---|
| Figure 1 | Hopper and Tray for Catching Spherules |
| Figure 2 | Laser Beam Focussing Head and Drill Motor |
| Figure 3 | Ceramic Rod Being Spun-Melted |
| Figure 4 | Yb_2O_3 Spherules |
| Figure 5 | Y_2O_3 Spherules |
| Figure 6 | Ca_2O_3 Spherules |
| Figure 7 | Possible Flow Diagram - Ground Operations |
| Figure 8 | Electrical Resistivity as a Function of Temperature for Some Oxides and Graphites |
| Figure 9 | Containerless Melting and Cooling - Preheating |
| Figure 10 | Containerless Melting and Cooling - Melting |
| Figure 11 | Containerless Melting and Cooling - Cooling |
| Figure 12 | Overall System Schematic |
| Figure 13 | Temperature Control Schematic |
| Figure 14 | Effect of Coil Coupling Efficiency on Power Required to Melt 1/2-inch Diameter Spheres of Al_2O_3 |
| Figure 15 | Possible Flight Operations Flow Diagram - Induction Melting |
| Figure 16 | Possible Flight Operations Flow Diagram - Laser Melting |
| Figure 17 | Calculated Cooling Curves for 1/2-inch Diameter Glass Spheres |
| Figure 18A | Master Plan Schedule - I. Optical Glasses for the Visible Spectrum |
| Figure 18B | Master Plan Schedule - II. Glasses for Applications Other than the Visible Spectrum |

INTRODUCTION AND SUMMARY

The combination of circumstances attending melting in space presents the possibility of making glasses from substances which to date have been observed only in the crystalline condition. The absence of a need for a solid container during the melting and superheating portion of the manufacturing cycle permits contamination-free melting, the only contact of the melt with its surroundings being a gaseous atmosphere or, if so desired, a vacuum. Thus it is possible to melt without contamination many high melting point materials that heretofore could not be successfully melted because of reaction with the melting crucible material. This advantage alone might permit the preparation of new substances as glasses if their viscosity is sufficiently high to suppress crystal growth on cooling. In addition, space melting permits cooling without requiring the use of a solid mold. Thus, many of the usual crystal nucleation sites are eliminated. Unless a given material can spontaneously nucleate on cooling, and this requires that a nucleation energy barrier be surmounted, super-cooling below the normal melting point will occur. If a sufficient amount of supercooling is obtained (i.e., below the glass transition temperature), crystallization will be avoided entirely, and glass will result. The concept of glassmaking in space is particularly intriguing for the following reasons:

1. There is a strong possibility that high melting oxides such as La_2O_3 , Nb_2O_5 , Al_2O_3 , Y_2O_3 , and some of the rare earth oxides can be prepared as glasses in commercially useful sized spherical boules through space melting and cooling.
2. Glasses produced from such oxides or combinations of them with other oxide additions should have optical properties not obtainable in the conventional silicate, borate, and phosphate-based glasses.

3. The combination of optical properties projected for such glasses should make them suitable for use in advanced optical systems.
4. The spherical shape of glass boules that would result naturally from space production is quite suitable for the making of lenses and windows.
5. The production of glass, given a well-engineered space facility, should be well within the capabilities of the astronauts after a suitable brief training period, the more technically and/or skill oriented operations being performed terrestrially before and after flight operations.
6. A well directed research and development program leading to the production of useful space glasses should yield much valuable scientific information on the nature of glass formation, nucleation theory, etc..

In addition to "unique" glasses, which may not be preparable in any but a zero gravity environment, there are types of conventional or near-conventional glasses whose properties might be improved by zero gravity processing. Some glasses are subject to stratification because of different composition (and density) zones in the glass solution. Others are subject to microphase separation. Space processing may result in significant improvement in the optical properties of such glasses since stratification should not occur in zero gravity.

It is envisioned that the process described will ultimately not be limited to oxide glasses. Perhaps other compounds such as carbides, nitrides, and chalcogenides will ultimately become producible as glasses by space processing. If pure elements such as germanium and silicon could be produced as glasses, significant applications might also develop for them.

To date the space glass program has by choice been confined to oxide glasses only. Lack of sufficient funds prohibits investigation of more than one family

of materials simultaneously. It is felt that the applications for oxide glasses are more readily predictable than for the other materials, and that many of the principles that will evolve from a study of oxide glasses permit a more directed approach to non-oxide materials in the future.

The present report presents the results of a six-months study under contract NAS8-28014. The report is organized into five major sections entitled:

1. Potential Applications for Unique Space-Produced Glasses
2. Glass Experiments
3. Process and Equipment Study
4. "Conventional" Glasses in Zero G
5. Future Work Plan

The first section summarizes the results of a study, performed under sub-contract, by the Optical Group of the Perkin-Elmer Corporation and their full report is included as an Appendix to this report.

The second section summarizes experimental work performed by the North American Rockwell Corporation Science Center under the direction of Dr. Leo Topol. A number of new oxide glasses have been prepared by a laser spin-melting technique where droplets are ejected from a molten mass of appropriate composition. Techniques have been developed for measuring the optical properties of most of the new glasses so produced.

The third section presents a summary of the results of a preliminary study of processing equipment for producing new glasses in a zero gravity environment in a manned space laboratory. Induction and laser melting emerge as preferred techniques for melting experimental-sized boules (spheroids) of new glass compositions in space. In addition the results of NR's studies on chambers, preheating, position control, and cooling are summarized. Sample calculations for power required to induction melt typical new glass compositions are presented in an appendix. The induction melting of 1/2-inch diameter samples of typical

new glasses appears well within the electrical power capabilities projected for scheduled manned laboratories. Cooling rate calculations show that radiation cooling the high melting materials studied results in very short cooling times (less than four seconds) for 1/2-inch diameters to temperatures where the boules may be handled.

The fourth section delineates areas where zero gravity melting may prove advantageous for improving the quality of some "conventional" glasses.

The final section presents a future work plan. A master plan is keyed to anticipated manned laboratory flight dates. A detailed plan for NASA FY 73 is presented in the last part of the section. Major emphasis is placed on a program of sounding rocket experiments to produce glass samples of sufficient size to assess size effects and to permit accurate property measurements.

POTENTIAL APPLICATIONS FOR UNIQUE SPACE-PRODUCED GLASSES

An applications study was performed under subcontract by the Perkin-Elmer Corporation, Optical Group, Norwalk, Connecticut. Perkin-Elmer's report, Engineering Report No. 10952, dated 15 February, 1972 to the contractor is included in its entirety as Appendix I to this report.

Possible applications for new, space-produced glasses include:

Non Imaging Applications

1. Windows for CO₂ lasers (high transmission at 10.6 microns)
2. Host materials for 1.06 micron lasers.
3. Raw materials (emitters) for coatings

Imaging Applications

1. Elements for multi-element lenses, especially high numerical aperture systems, where new combinations of refractive index and dispersion could result in needed improvements in achromatization and secondary spectrum corrections.
 - a. Microscope objectives
 - b. Low light level lenses
 - c. Long focal length lenses for reconnaissance and astronomical systems
2. Elements for multi-element lenses where high index of refraction could be used to advantage.
 - a. Anastigmatic photographic objectives (to obtain a flat field, free of astigmatism)
 - b. Aplanats (lenses corrected for spherical aberrations and coma)

c. Components with better characteristics because of elements with lower curvatures

- (1) Zoom lenses
- (2) Spectrometers
- (3) Monochromators
- (4) Polarizing microscope components
- (5) High speed, large sized lenses

d. High numerical aperture systems

- (1) Oil immersion microscope objectives
- (2) Fiber optics bundles

It should be recognized that too little work has been done to date to permit an accurate prediction whether such applications will materialize. Much more information is needed on optical and physical properties of the new glasses and the range of properties obtainable in order to pin down specific applications. Nevertheless, it would appear that the potential is there and if only a relatively small portion of the potential applications area, as outlined by Perkin-Elmer, materializes the ultimate production of glasses in space will have been justified.

It should also be noted that most of the potential applications described in Appendix I are for sophisticated, expensive systems where the relatively high cost of space production should not be a deterrent to the use of space-produced glasses.

GLASS EXPERIMENTS

Experimental work, performed by personnel of the North American Rockwell Corporation Science Center utilized laser melting of spinning rods made by pressing and sintering pure or mixed oxides of appropriate proportions. Small droplets were spun off from the molten ends of the rods and were allowed to free-fall cool. The resultant spherules were examined microscopically with white light and under a polarizing analyzer to determine whether they were glassy, crystalline, or a combination. A significant portion of the experimental work was devoted to developing techniques for measuring the optical properties of the glassy spherules produced.

CHOICE OF SYSTEMS

For the present glass formation studies, various oxides with appropriate optical and physical properties have been considered. A list of these are presented in Table 1. Among these oxides are Al_2O_3 , La_2O_3 , Ta_2O_5 and Nb_2O_5 all of which have yielded glasses with various CaO additions in our previous investigations. Because of the success with the above, emphasis was placed on those oxides that are chemically related to Al_2O_3 and La_2O_3 . (The remaining group Va oxide, V_2O_5 , unlike Nb_2O_5 and Ta_2O_5 , was not considered due to its low melting point and instability at higher temperatures.) Thus, the Al_2O_3 - related Ga_2O_3 (In_2O_3 was omitted due to its apparent volatility) and the La_2O_3 - like Sc_2O_3 , Y_2O_3 and several rare earth oxides were chosen. Since MgO , ZnO , PbO , WO_3 and TiO_2 in high concentration can be added to many glasses, these as well as ZrO_2 and HfO_2 (being in the same group as TiO_2) were included. Finally, SnO and Bi_2O_3 were considered since they are related to known glass formers, the former to SiO_2 and GeO_2 and the latter, Bi_2O_3 , to arsenic and antimony oxides.

From the above list, the following pure oxides were chosen: Ga_2O_3 , Y_2O_3 , La_2O_3 , Sm_2O_3 , Gd_2O_3 , Yb_2O_3 , Lu_2O_3 , TiO_2 , WO_3 , MgO and ZnO . Volatility

Enclosure

Table I. Candidate Oxides

<u>Oxide</u>	<u>Approx. Melting Point, °C</u>	<u>Boiling Point, °C</u>	<u>n_D</u>	<u>Relative (1) Stability</u>	<u>Color</u>
Al ₂ O ₃	2070	2980	1.76/1.77	V.S.	White
Bi ₂ O ₃	830	1900(?)	1.9	S.	Wh-Yel.-V.Volatile ⁽²⁾
Ga ₂ O ₃	1800	-	1.9	V.S.	Colorless
Gd ₂ O ₃	2330	-	-	hyg.	White
HfO ₂	2900	~5400(?)	2.1	V.S.	White
La ₂ O ₃	2310	4200	-	hyg.	White
Lu ₂ O ₃	-	-	-	?	Wh.-Colorless
MgO	2850	3600	1.7379	V.S.	White
Nb ₂ O ₅	1490	-	2.258	?	White
PbO	886	1472	2.6	S.	Yel.-V.Volatile
Sc ₂ O ₃	>2405	-	-	?	White
Sm ₂ O ₃	~2350	-	-	?	Wh.-Yel.
SnO ₂	1630	1800-1900 (Subl.)	2.0	S.	White-Volatile
Ta ₂ O ₅	1870	>2200	2.09	V.S.	Colorless
TiO ₂	1845	-O ₂ @ 1900	2.6/2.9	?	Colorless (rut.)
WO ₃	1470	>2200	-	?	Yellow
Y ₂ O ₃	2410	~4300	-	?	Colorless-Yel.
Yb ₂ O ₃	2250	-	-	?	Colorless
AnO	1970	-	2.01/2.03	V.S.	White
ZrO ₂	2690	~4300	2.13-2.20	V.S.	White

(1) V.S. = very stable
 S. = stable
 hyg. = hygroscopic

(2) v = very

considerations eliminated PbO , Bi_2O_3 and SnO_2 , while repetition of previous runs, performed prior to the awarding of the present contract, with Al_2O_3 , ZrO_2 , HfO_2 , Nb_2O_5 and Ta_2O_5 was not deemed worthwhile at present. Since no optical measurements were made on the glasses produced from La_2O_3 due to its hygroscopicity, this system was repeated. From our experience and knowledge of glass formation, the simple oxides most likely to be successful are those like La_2O_3 . Binary compositions of the spinel $\text{MgO} \cdot \text{Al}_2\text{O}_3$ as well as each of the following with 10 and 20 wt % CaO were also prepared: Ga_2O_3 , Y_2O_3 , Sm_2O_3 , Gd_2O_3 and Lu_2O_3 . In addition, some rods of Y_2O_3 and Ta_2O_5 with the CaO replaced by BaO and Ta_2O_5 + 10% ZnO composition were also tested. The BaO and ZnO ceramics should yield higher refractive index glasses than the corresponding CaO ones. The above binary compositions were chosen for their potential as glass formers as well as their possible optical properties.

EXPERIMENTAL

A 250 watt continuous wave CO_2 laser (Model 41, Coherent Radiation Laboratories, Palo Alto, Calif.) operating at 10.6 microns was used as the heat source. The beam was focused downward with gallium arsenide lenses of 6.35 cm or 12.7 cm focal length onto the end of the specimen in the form of a rod. Since the laser unit utilizes a gas jet to protect its lens from impinging objects, the flow of gas (oxygen in our runs) had to be minimized. The ceramic rods were about 3 mm in diameter and were hot pressed from uniformly blended mixtures of high purity chosen oxide compositions by the Haselden Co., San Jose, Calif.

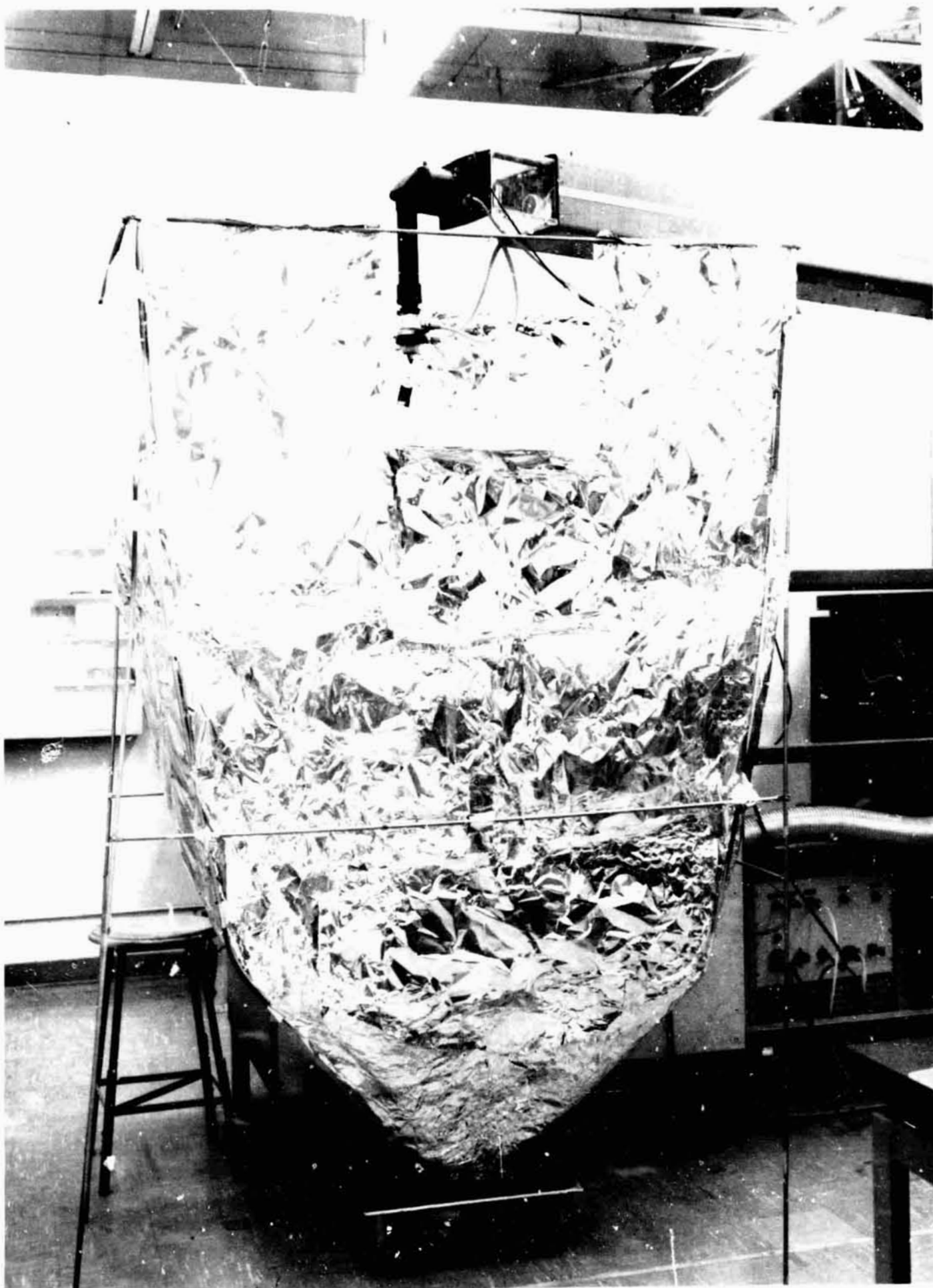
The technique employed to produce glass spherules was to place the ceramic rods in a high-speed drill and rotate them at a known speed of 8,000 to 30,000 rpm. The face and tip of the spinning rod were then introduced into the laser beam and molten droplets were spun off. These varied in size from about 100 μm to 800 μm depending on the material, the speed of rotation and the laser beam power density.

With the 6.35 cm lens a beam power of 250-300 watts and spin speed of 20,000 rpm usually gave an optimum yield. With the 12.7 cm lens the beam power could be reduced to 200 watts. The spherules were caught in a large funnel-shaped aluminum foil hopper and collected in a stainless steel tray. (See Figure 1). The spherules were then transferred into small plastic boxes and were examined microscopically to determine the optimum parameters.

Figure 2 shows the details of the laser beam focusing head and the variable speed drill motor with the ceramic rod about to be introduced into the beam path. Figure 3 is a time exposure showing a ceramic rod ($\text{MgO} - \text{SiO}_2$) in the process of being spun under the laser beam at about 10,000 rpm. The traces of the ejected molten droplets are clearly visible.

Mixtures tested in this study were composed of 80, 90 and 100 wt % Sm_2O_3 ; 80, 90 and 100% Gd_2O_3 ; 80, 90 and 100% Ca_2O_3 ; 80, 90 and 100% Y_2O_3 ; 90 and 100% La_2O_3 with the other component in each case being CaO ; Yb_2O_3 ; 90% Yb_2O_3 ; 80 and 90% Ta_2O_5 with the remainder in these systems being BaO ; 90% Ta_2O_5 + 10% ZnO ; ZnO ; MgO ; $\text{MgO} \cdot \text{Al}_2\text{O}_3$; and TiO_2 .

These spherules which were clear and smooth were immersed in liquid of appropriate refractive index and checked by microscopic examination with polarized light and crossed nicols. This procedure distinguishes glass from all crystalline materials except those of cubic structure. The index of refraction, n , and the dispersion, $dn/d\lambda$, of the glassy spherules were then determined. For indices of refraction less than 2.0, standard immersion liquids and the central as well as oblique illumination methods were utilized. It should be pointed out that since the specimens were spheres, the apparent Becke line at the specimen-liquid interface proved to be misleading by the central illumination technique. Instead, the increase or decrease of the light interior area of the sphere or,



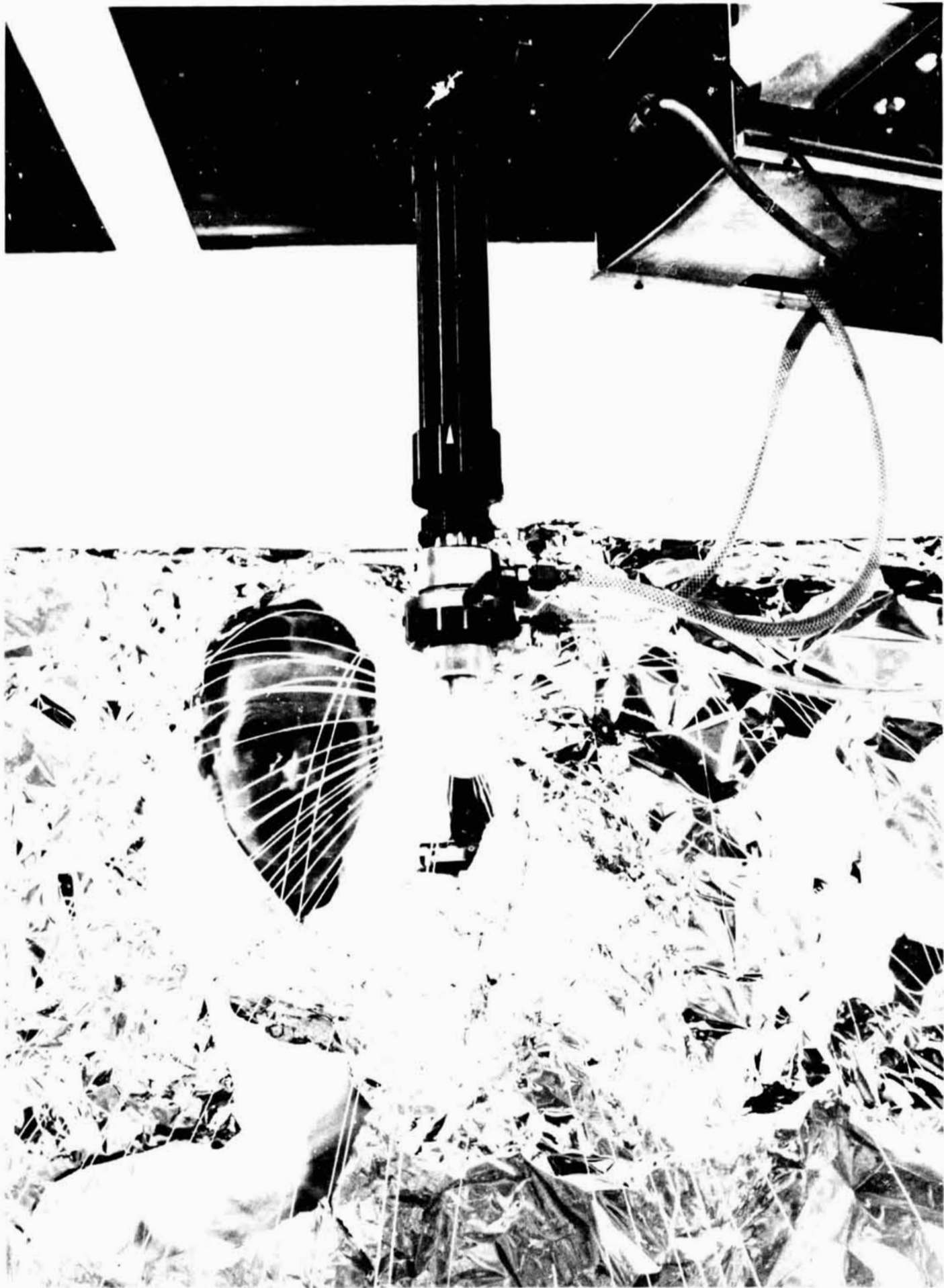
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Figure 1 HOPPER AND TRAY FOR CATCHING SPHERULES



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Figure 2 LASER BEAM FOCUSING HEAD AND DRILL MOTOR



700-86-1074D

Figure 3 CERAMIC ROD BEING SPUN-MELTED

conversely, the decrease or increase of the dark border at the circumference of the sphere as the distance between the specimen and microscope lens is increased showed that the liquid or sphere, respectively, had the higher refractive index. With the oblique illumination method the results were straightforward. Here, as an opaque stop is gradually inserted into the optical light path, the shadow will fall on the edge of the object on the same side as the approaching stop if the object has a higher refractive index than the immersion liquid and vice versa. Indices were measured at 589, 656 and 486 μ with the aid of interference filters and a Zeiss microrefractometer. The microrefractometer was used to measure the indices of the liquids after the latter had been matched with a glass sample at a specific wavelength. Since the microrefractometer has an upper measuring limit of 2.00 and also since the immersion liquids commercially available in the range 2.00-2.11 only give the index value at 589 μ , other techniques had to be employed to measure indices at the other wavelengths as well as for higher values, i.e., n greater than 2.11. For glasses with $n \geq 2.00$, solid immersion media and microscopic measurement of the displacement of the image, e.g., the deChaulnes method, were also utilized. The latter method involves measuring the true thickness and the apparent or optical thickness of the sample; the ratio of the two yields n . The thicknesses were measured with an indicator gauge mounted on the microscope and in contact with the movable stage. The gauge has a travel distance of about 1.25 cm and is marked off in 1×10^{-4} in. (2.5×10^{-4} cm) units but can be read to about $\pm 5 \times 10^{-5}$ cm. To facilitate matters, the spherules had two parallel flats polished on them and a scratched platinum-coated slide served as a focusing target.* For solid immersion media, S-Se melts¹ for the range of $n=2.0$ -2.5 as well as pressed

* As suggested by Dr. H. Osterberg of the American Optical Company

(1) H. E. Merwin and E. S. Larsen, Amer. J. Sci. 34, 42 (1912)

solid solution pellets of AgCl + AgBr for n_D of 2.06-2.25 were employed. The n values for several AgCl-AgBr compositions were determined by the deChaulnes method. When the silver halides were used, thin discs were machined from single crystal boules prepared by the Bridgman-Stockbarger technique. The spherule was then pressed into the halide pellet in a 6.35 mm I.D. pressure die and viewed with the spherule-air side downward immersed in a high index liquid. The liquid served to minimize the high contrast at the sphere-air interface and maximized light transmission through the medium. However, a set of standard solids, covering the range 2.12-2.30 for n_D was recently purchased from R. P. Gargille Laboratories, Inc. (Cedar Grove, N. J.), and all the n_D values reported are based on these. Although the above procedures for $n > 2.0$ are cumbersome and tedious, other possible techniques appear to have equal disadvantages. Some of these other candidate methods that have also been considered are: (1) the use of transmission measurements², (2) the use of diffuse reflectance³ from a large number of spheres, (3) transmission interference microscopy with polarized light⁴, (4) the "rainbow" technique⁵, where dispersion is measured directly by breaking white light into its components, analagous to the similar case with raindrops, and (5) the use of a high index refractometer.⁶

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- (2) K. Kapadopoulos, C. C. Chen, and G. J. Su, Physics Chem. Glasses 11, 18 (1970).
 - (3) E. L. Simmons, Optica Acta 18, 59 (1971); and N. T. Melamed, Appl. Phys. 34, 560 (1963).
 - (4) H. Piller, Sonderdruck Zeiss-Mitteilungen 2, 309, (1962)
 - (5) A. Walther "Optical Applications of Solid Glass Spheres" - Thesis, University of Del't, Holland (1959) - Published by Diffraction Limited, Inc., Bedford, Mass.
 - (6) A. H. Pfund, J. Opt. Soc. Am. 39, 966 (1949); H. Haacke and J. Hartmann, Optik 11, 380 (1954).

The first procedure would require the measurement of light corrected for absorption through a parallel-sided specimen. This would require the use of several spherules with polished parallel flat faces of various thickness and a method of accurately (to $\pm 0.5\%$) measuring the transmission. For values of $n = 2.0$ the error would be ± 0.015 in the index value. In the second procedure, diffuse reflectance, a large number of uniform spheres must be available and the average diameter as well as absorption coefficient must be known. The errors in the measurements as well as in the assumptions involved in the derivation are greater than 1% (or ± 0.02 in n). The third procedure involves the immersion of the sample in a medium of known index and measuring the phase changes in the polarized light transmitted. However, it is not clear how the procedure works since only the phase change (up to 2π) can be measured and not the integral number of changes, i.e., $m\pi$. In the equations given in the reference, the latter quantity, m , was not considered and it appears that the procedure is extremely limited in use, i.e., for samples of thickness of the order of the wavelength of light or for immersion media or n very similar to that of the sample. The "rainbow" procedure was attempted using individual glass spherules and a laser source. Results were unsatisfactory, however, presumably due to surface irregularities and the small size of the spherules. Lastly, the Pfund refractometer involves the use of a hemisphere of high known refractive material in optical contact with an unknown sample and measuring the angle where Newton's rings disappear at the contact interface. For hemisphere material, rutile (TiO_2) or SrTiO_3 can be used. This method should produce the most accurate data but as with the other procedures above, it would involve a long induction period to set up and perfect.

RESULTS AND DISCUSSION

Approximately a hundred spherules of each of the compositions tested were collected. A large variety of samples were obtained ranging from those which were obviously crystalline to clear, smooth spherules. The clear, spherical (or ellipsoidal

in one system), smooth-surfaced specimens were invariably glass (except for some of the pure lanthanide oxides).

Clear spherules with a fairly smooth surface having some irregularities generally had a glass interior and a crystalline surface. Translucent spherules were, generally, very finely crystalline and resembled a finely devitrified glass in the microscope. Specimens which had non-spherical, irregular or lumpy surfaces were generally crystalline.

Some glass spheres were produced with about 2/3 of the compositions tried and with many compositions more than 10% of the spherules were glass.

Figures 4-6 show three of the compositions which yielded large fractions of glass, Yb_2O_3 , Y_2O_3 and $\text{Ga}_2\text{O}_3 + 20\% \text{CaO}$. The lines in the plates are 1/64" (0.4mm) apart. With the Yb_2O_3 and Y_2O_3 some hemispheres are present, apparently caused by splitting of the spheres due to high stress present during the glass formation. With the $\text{Ga}_2\text{O}_3 + \text{CaO}$ mixture some ellipsoidal glass forms are present. The textures of the spherules range from clear, smooth glass to milky translucent microcrystalline, to opaque white, fine-grained crystalline to relatively coarse-grained, translucent crystalline lumpy spheres. The Ga_2O_3 - based glasses are seen to contain numerous bubbles (see Figure 3).

Table II lists the compositions studied and summarizes the experimental results. The lanthanide oxides formed light brown to orange to colorless spherules and it is not known if impurities or suboxide formation is the cause of the color. Further, the La_2O_3 , Sm_2O_3 and Gd_2O_3 spherules between crossed nicols showed a great deal of microcrystalline phases to be present as indicated in the table. The La_2O_3 spherules deteriorated to a powder in a few days in air or in two weeks in a desiccator. X-ray analysis of the white powder showed the presence of hydroxide. Another interesting point with the lanthanide oxides is that the glass yield decreased as CaO was added in contrast to the effect with virtually all the other oxides where glass-forming ability is poor but increases with added CaO .

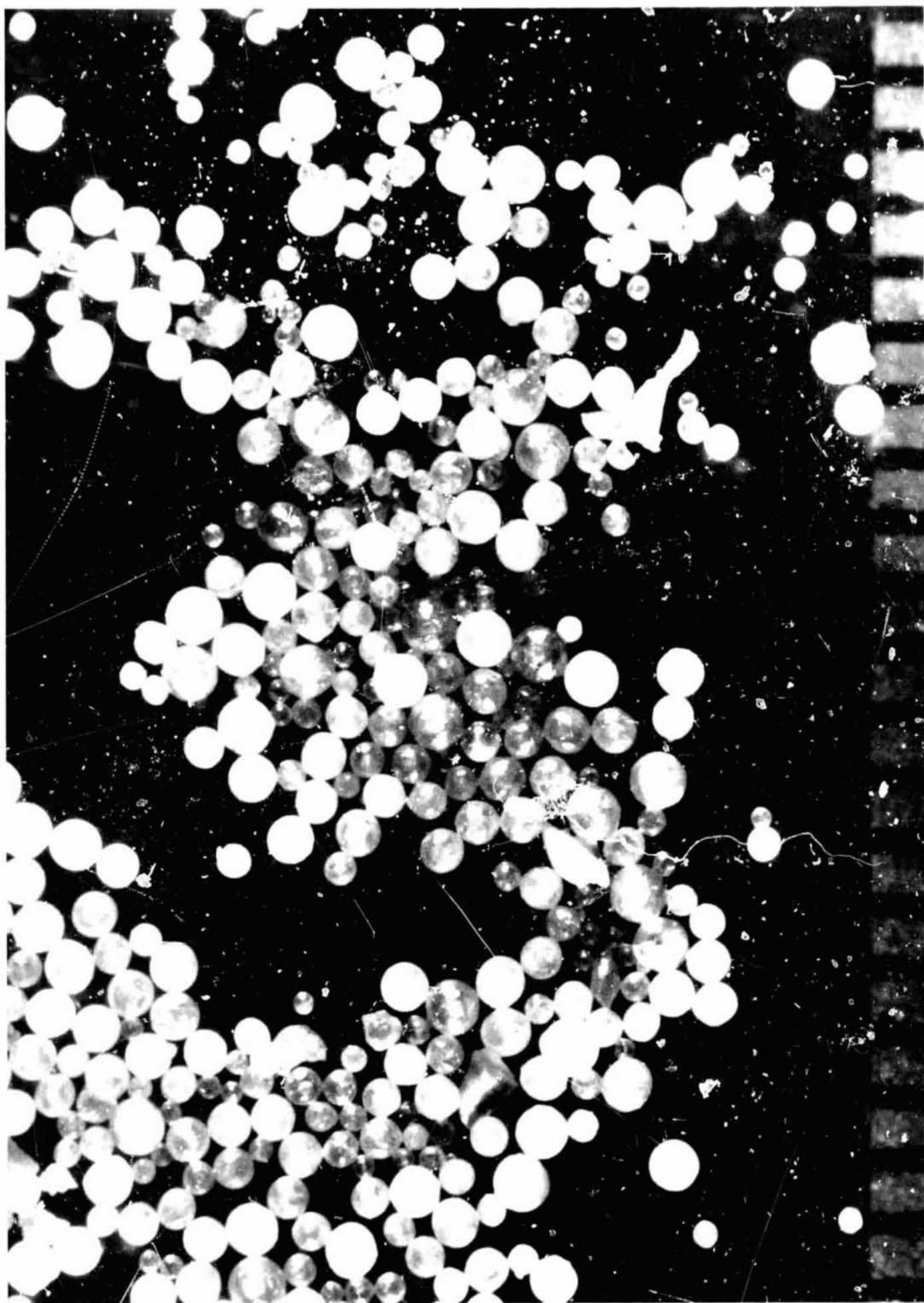


Figure 4 Yb_2O_3 Spherules (Scale = 0.4 μm .)

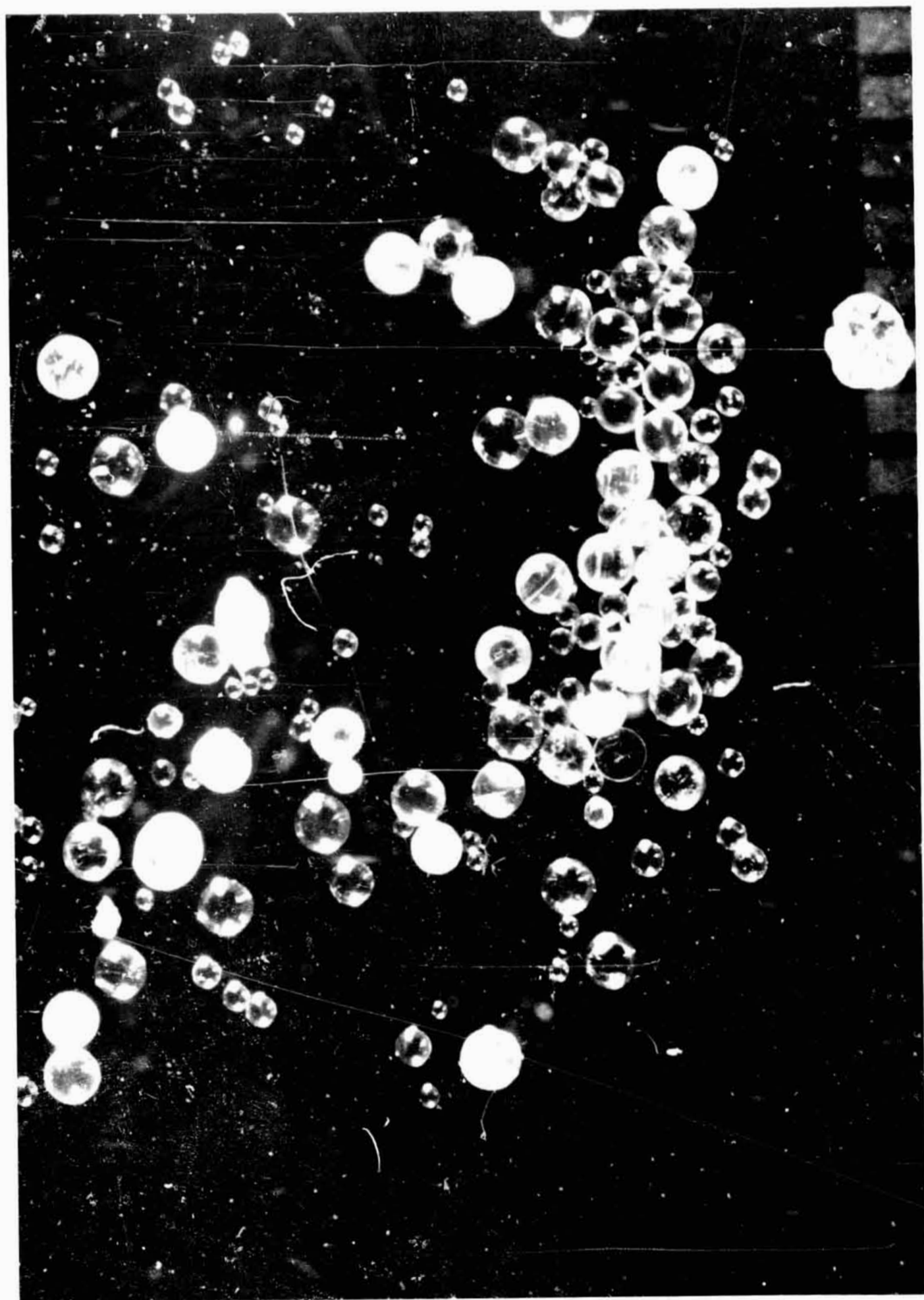


Figure 5 Y_2O_3 Spherules (Scale = 0.4 mm.)

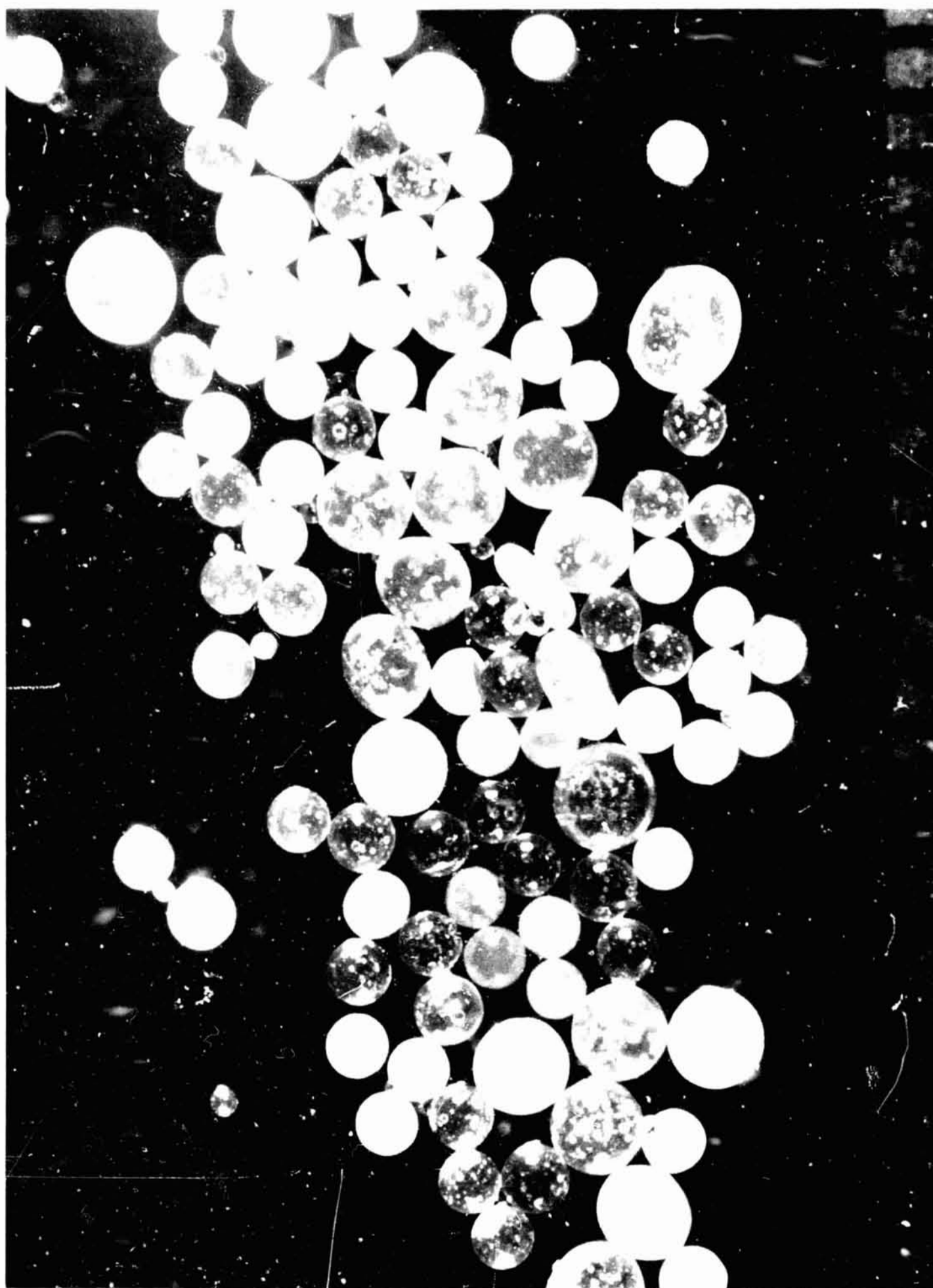


Figure 6 Ga_2O_3 + 20 wt. % CaO Spherules (Scale = 0.4 mm.)

Table II
Results of Laser Melting Experiments

Major Constituent	% CaO	Rating*	Specific Observations
La ₂ O ₃	-	++	0-10% yield; brown to colorless; devitrified in 2 weeks in desiccator.
La ₂ O ₃	10	+	0-1% yield; brown to colorless; microcrystalline phases.
Yb ₂ O ₃	-	+++	50-95%; colorless, pale brown; pure glass predominates; some hemispheres present.
Sm ₂ O ₃	-	+++	50-80%, if small; color variable; microcrystalline phases.
Sm ₂ O ₃	10	++	0-10%; fair quality; color variable; microcrystalline phases.
Sm ₂ O ₃	20	+	0-1%; fair quality; microcrystalline phases.
Gd ₂ O ₃	-	+++	50-90%; tend to be clearer than Sm ₂ O ₃ ; variable color; some microcrystalline phases.
Gd ₂ O ₃	10	++	0-10%; fair quality; microcrystalline phases.
Gd ₂ O ₃	20	+	0-2%; fair quality; microcrystalline phases.
MgO	-	0	
Ga ₂ O ₃	-	++	0-2%; few good glass; possible microcrystalline material in the glass; some fair quality spheres.
Ga ₂ O ₃	10	+	0-1%; a few are pure glass; most microcrystalline phases.
Ga ₂ O ₃	20	+++	20-70%; some pure glass; some elliptical.
Y ₂ O ₃	-	+++	20-100%; many pure glass; striated surface; hemispheres; some pale brown.
Y ₂ O ₃	10	+++	10-50%; some pure glass; most fair with microcrystalline phases.
Y ₂ O ₃	20	++	0-10%; few are good; most fair.
Y ₂ O ₃	10 BaO	+ ?	Few (< 1%) fair glass; microcrystalline phases.

Table II. Results of Laser Melting Experiments (Continued)

Major Constituent	% CaO	Rating	Specific Observations
Ta ₂ O ₅	10 ZnO	0	Perhaps trace of fair quality glass.
ZnO	-	0 ?	Perhaps a trace of glass in spheres, but of poor quality; volatile.
WO ₃	-	0	Volatile.
TiO ₂	-	0	
Ta ₂ O ₅	10% BaO	0	Perhaps trace of glass.
Ta ₂ O ₅	20% BaO	0	

* +++ Glass > 10 percent of total
 ++ 10 percent > glass > 1 percent
 + 1 percent > glass > 0 percent
 0 No glass observed

For the other systems the substitution of BaO for CaO with Y_2O_3 and Ta_2O_5 , two good glass-forming oxides, and also of ZnO with Ta_2O_5 yielded no glass. Specificity or ionic size may be important here. The volatility of ZnO and WO_3 makes their use as glass formers under the present conditions very difficult. Mixing these with CaO may abet glass formation. The TiO_2 yielded mainly dark opaque material but also some light matter. This suggests that different valence states of Ti are present. Note that TiO_2 starts losing oxygen above its melting point.

The optical properties in the visible of all the glasses measured in this study are reported in Table III. Thus, several of the glasses prepared previously are also included. The optical properties determined consist of the index of refraction at 589mμ, n_D , and the Abbe number ν , an inverse measure of the dispersion

$$\nu = \frac{n_D - 1}{n_{486} - n_{656}}$$

The precision of the n_D values is ± 0.003 for $n_D \leq 1.80$ and ± 0.01 for $n_D > 1.80$. In two $Ta_2O_5 + 20\% CaO$ samples the Abbe numbers were determined by using both liquid immersion media and the deChaulnes method. In one case a sphere was used and in the other a specimen with two plane parallel faces polished on it. For a sphere of index n immersed in a liquid of index n_0 the index is given by

$$n = 2 n_0 - d/a$$

where d = diameter of the sphere

a = apparent diameter

and $n > n_0$.

For planar objects

$$n = d/a$$

and is independent of the immersion liquid used, if any. The agreement between the ν values for the $Ta_2O_5 - CaO$ is good especially since the sphere is much

Table III

INDEX OF REFRACTION AND DISPERSION OF OXIDE GLASSES

Composition (1)	n_D	Abbe Number	
		Liquid	Micros.
Y_2O_3	1.920	20	
$Y_2O_2 + 10\% CaO$	1.920 (?)		
$Y_2O_3 + 20\% CaO$	1.920 (?)		
$Y_2O_3 + 10\% BaO$	1.920 (?)		
La_2O_3	2.2 ± 0.1		
$La_2O_3 + 10\% CaO$	> 2.1		
Sm_2O_3	2.12		
$Sm_2O_3 + 10\% CaO$	2.04		
Gd_2O_3	2.09		
$Gd_2O_3 + 10\% CaO$	2.07		
Yb_2O_3	1.938	25	
Ga_2O_3	1.91	25	
$Ga_2O_3 + 10\% CaO$	1.852	25	
$Ga_2O_3 + 20\% CaO$	1.794	25	
$Al_2O_3 + 5\% SiO_2$	1.728	33	
$Al_2O_3 + 10\% SiO_2$	1.720	36	
$Al_2O_3 + 15\% SiO_2$	1.634	45	
$Al_2O_3 + 20\% SiO_2$	1.629	39	
$Al_2O_3 + 10\% CaO$	1.650	50	
$Al_2O_3 + 20\% CaO$	1.642	38	
$Al_2O_3 + 10\% SiO_2 + 10\% CaO$	1.632	37	
$Ta_2O_5 + 10\% CaO$	2.11		
$Ta_2O_5 + 20\% CaO$ (sphere)	1.95	20	17
$Ta_2O_5 + 20\% CaO$ (planar)	1.95	30	25

(1) Percentages are Weight Percent

Table III. INDEX OF REFRACTION AND DISPERSION OF OXIDE GLASSES (Continued)

Composition ⁽¹⁾	n_D	Abbe Number	
		Liquid	Micros.
Nb_2O_5 + 15% CaO	2.19		
Nb_2O_5 + 20% CaO	2.13		
Nb_2O_5 + 5% SiO_2	2.19		
Nb_2O_5 + 10% CaO + 5% SiO_2	2.18		
Nb_2O_5 + 10% CaO + 10% SiO_2	2.16		

(1) Percentages are Weight Percent

more difficult to measure due to spherical aberration, etc.

The identical n_D values for the different Y_2O_3 systems gives cause for suspicion. It suggests that the glass spherules are all pure or virtually pure Y_2O_3 . The systems with the highest indices of refraction are the Nb_2O_5 and La_2O_3 . The latter was uniquely difficult to measure for some reason but appears to be in the range 2.2 ± 0.1 .

The index of refraction is given by the Clausius-Mossotti and Lorenz-Lorentz (C-M, L-L) relations⁷

$$\frac{n^2-1}{n^2+2} = \frac{4\pi Np}{3 V_m}$$

where N is Avogadro's number

p = polarizability (electronic)

and V_m = molar volume of the oxide = M/p .

In the above equation the atomic polarizability has been ignored. From this relation with the measured or extrapolated (for Al_2O_3 , Nb_2O_5 and Ta_2O_5) indices and the known densities⁸ of the crystalline oxides, values of p can be calculated.

Since p is proportional to the cube of the radius of the molecule M_aO_b , it may be level with compared with the values $\sum (ar_M^3 + br_O^3)$ where r_M and r_O are the crystal radii⁸ of the cation M and oxide ion, 1.32×10^{-8} cm, respectively. These data are given in Table IV and suggest that the polarizabilities of the oxide ion in the Al_2O_3 and Ga_2O_3 systems are much less than in the others. Further, according to the C-M, L-L relation the trend in refractive index should be given by $(ar_M^3 + br_O^3)/V_m$. However, tabulation of these values does not show any meaningful correspondence with the measured refractive indices. Actually, the trend in n for oxides of cations of

(7) See W. J. Moore, Physical Chemistry, Prentice-Hall, Inc., 1962

(8) Handbook of Chemistry and Physics, The Chemical Rubber Co., Cleveland, Ohio, 1968

Comparison of Calculated Polarizabilities with (Radius)³ for Metal Oxide (M_aO_b) Glasses

Oxide	V _m ⁽¹⁾ (ml)	r _M × 10 ⁸ (2) (cm)	n _D	p × 10 ²⁴ (ml)	Σ(ar _M ³ + br _O ³) ⁽²⁾ × 10 ²⁴ (ml)	Σ(ar _M ³ + br _O ³)/V _m × 10 ²⁴ ⁽²⁾
Y ₂ O ₃	45.3	0.893	1.92	8.50	8.33	0.18
La ₂ O ₃	50.0	1.016	(2.20)	11.1	9.00	0.180
Sm ₂ O ₃	41.9	0.964	2.12	8.94	8.69	0.207
Gd ₂ O ₃	49.0	0.938	2.09	10.27	8.55	0.175
Yb ₂ O ₃	42.9	0.858	1.94	8.16	8.16	0.190
Al ₂ O ₃	25.6	0.51	(1.73)	4.1	7.17	0.280
Ga ₂ O ₃	29.4	0.62	1.91	5.48	7.38	0.251
Nb ₂ O ₅	59.5	0.69	(2.25)	13.6	12.16	0.204
Ta ₂ O ₅	54.0	0.68	(2.20)	12.0	12.13	0.225

(1) Molar volume of crystalline oxide.

(2) Ionic radius; for oxide ion r is taken as 1.32 × 10⁻⁸ cm.

similar groups appears to be most predictable from the cation radius alone. More data are required before any validity in a trend between n and r_M can be firmly established for different subgroups and families of metals.

The results of these experiments show that Y_2O_3 , pure or with 10 wt % CaO, $Ga_2O_3 + 20\% CaO$ and pure Yb_2O_3 are good glass formers with the laser melting procedure and should be considered as candidates for future experiments in space. From these results, it would appear that pure Lu_2O_3 and $Sc_2O_3 + CaO$, yet to be tested, should also fall in this category.

SUMMARY

In addition to the La_2O_3 and Ta_2O_5 - and Nb_2O_5 - based systems, which yielded glasses in the previously performed NR-funded program, it has been demonstrated in the present study that glasses can be obtained from pure Y_2O_3 , Sm_2O_3 , Gd_2O_3 , Yb_2O_3 and compositions rich in Ga_2O_3 .

Techniques for measuring the index of refraction and Abbe numbers of the small spherules produced by the laser spin-melting technique. Time did not permit Abbe number measurements on all of the glasses produced on this program, however.

PROCESS AND EQUIPMENT STUDY

Approximately 7% of the contract effort was devoted to a process and equipment study leading to a pointing of the way for future studies in connection with manned orbital missions. During this study an attempt was made to comply with the theoretical requirements for optimum melting of unique oxide glasses in space. These "requirements" as presently foreseen are listed below.

- 1) Starting material must be oxides of the highest purity obtainable.
- 2) Because of the difficulty of removing bubbles in zero gravity, volatile content of the starting rods or slugs must be as low as possible. In addition to starting with pure oxides only (rather than the oxides, fluorides, nitrates, carbonates, etc. used in conventional glass manufacture) the starting material in the form of pressed and sintered slugs or rods must be vacuum outgassed and then stored so as to prevent re-introduction of gas.
- 3) In order to achieve rapid cooling rates using radiation cooling, melting temperatures should be as high as possible. In order to prevent formation of bubbles during melting, boiling points of all constituents should also be as high as possible.
- 4) While many of the oxides being considered are quite stable and theoretically can be melted in vacuum or in an inert atmosphere, others are relatively unstable and/or can form suboxides or can contain less than stoichiometric amounts of oxygen, for example TiO_2 which, unless melted under oxidizing conditions will contain less than stoichiometric amount of oxygen. This leads to the formation of color centers and loss of

transparency in a glass formed from a composition of high TiO_2 content. While it might be possible to restore oxygen by heat treating the glass in oxygen, there is a strong risk that devitrification temperatures and temperatures where diffusion rates are adequate might be incompatible. Therefore, space melting equipment, if it is to be capable of handling the entire range of oxide optical glasses with potentially attractive properties, should be so designed as to permit melting under an air or preferably pure oxygen atmosphere. The writer knows of no superoxides containing more than stoichiometric amounts of oxygen, so that there appears to be little risk of damaging glasses with an excess of oxygen. A possible exception to this is where the desired glass is of a sub-oxide composition, for example silicon monoxide, SiO . In such a case, careful consideration would have to be given to maintaining a stoichiometric oxygen content. To date, such sub-oxide glasses have not been seriously considered.

5) In order to destroy residual crystalline nuclei that might remain in the molten oxide, the melt should be superheated at least 200°C above its melting point. It would, of course, be preferable to be able to do this with nothing but the surrounding atmosphere in contact with the molten spheroid, to preclude the possibility of spalling of crystalline fragments into the melt. For this reason, direct resistance melting* was eliminated from the present study even though it is attractive from many points of view and undoubtedly could be used for the better glass forming compositions.

6) The equipment should be so designed as to be capable of preventing contact of the molten or cooling spheroid with solid surfaces until the

* For further discussion of resistance melting for sounding rocket experiments, see section entitled, "FUTURE WORK PLAN".

glass transition temperature has been reached on cooling. More will be said about position control later.

7) Finally, in order to prevent cracking or unacceptably high residual stress, it might be necessary to retard cooling, especially in the case of glasses with high expansion coefficients. The equipment should be capable of providing slower-than-maximum cooling rates in the glass spheroid.

In the present study, seven basic melting methods were considered as follows: 1) induction, 2) laser, 3) electrical resistance furnace, 4) electron beam, 5) direct solar heating (solar furnace), 6) chemical, such as gas flames and reactions and 7) electric arcs. Each of the seven methods will be discussed separately. Since early in this study induction and laser appeared to be the preferred methods for experimental melting, more effort was expended on them than on the others.

Some thought also was given to chamber design, pre-heating (for induction and possibly for electron beam melting), cooling, and position control. Subsequent sections will discuss these.

The basic process visualized for pre-flight and post-flight (ground) operations is summarized in Figure 7.

BASIC MELTING METHODS

Induction

Induction melting appears to be an almost ideal method for containerless melting of glass in space. The method is safe and clean; is not significantly affected by the atmosphere (the coils are fluid cooled); can produce temperatures in the required range; and there is no physical contact with the object being heated. The process has been extensively used (but not for glass melting) and a high degree of state-of-the-art has been achieved. Only a moderate amount of skill is required to operate induction units once the set-up has been worked out. Another possible advantage is that positioning

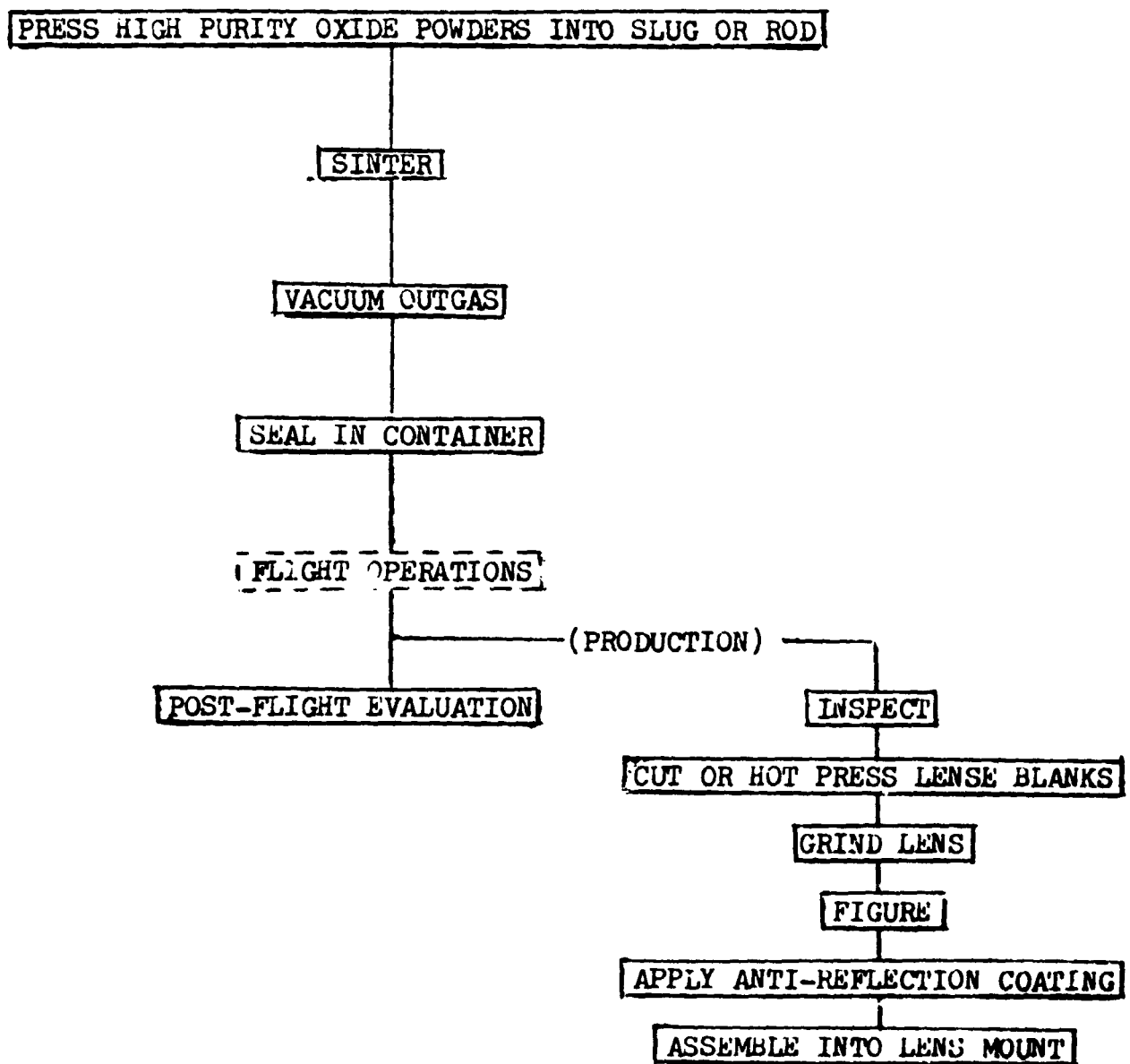


Figure 7 POSSIBLE FLOW DIAGRAM -- GROUND OPERATIONS

control might be achievable using an orthogonal or other suitable coil arrangement, although this has not been demonstrated to date.

In order for induction to work for glasses in space the glasses must be somewhat conductive. In Figure 3 are plotted the electrical resistivity vs. temperature for a number of oxides similar to those being considered for unique glasses. The graphites, with resistivities of about 10^{-3} ohm-cm. are commonly used as induction susceptors. ZrO_2 with a resistivity in the 10^{-1} to 10 ohm-cm. range is also known to be a satisfactory susceptor. It would appear, then, that all of the oxides in Figure 8, with the possible exception of Al_2O_3 and possibly MgO , will have resistivities at elevated temperatures such that they should be satisfactory induction susceptors. Of course, it will be necessary to preheat them, and this will be treated in a later section. Preheating will be required for induction, direct resistance melting, and possibly for electron beam melting (to provide a ground or return circuit). Of course, experimental work will have to be done to confirm that the specific compositions to be considered for preparing glasses in space are satisfactory susceptors. Probably those that are not can be rendered sufficiently conducting for induction melting by doping them with small quantities of oxide addition agents that, hopefully, will not significantly affect their usefulness as glass.

One unfortunate shortcoming of induction is electrical efficiency. Typical coil coupling efficiencies are about 20% and efficiencies in induction generators are in the 60 to 80% range. Thus efficiencies as low as 12% ($.60 \times .20 \times 100$) can be expected. In view of the weight problems with flight vehicles such low efficiencies are a pity. However competing process appear no better. Since the lion's share of the heating energy required serves to overcome radiation losses, considerable improvement in electrical consumption can be achieved by reflecting radiated energy back into the melt. Figures 9

ELECTRICAL RESISTIVITY AS A FUNCTION OF TEMPERATURE FOR SOME OXIDES & GRAPHITES

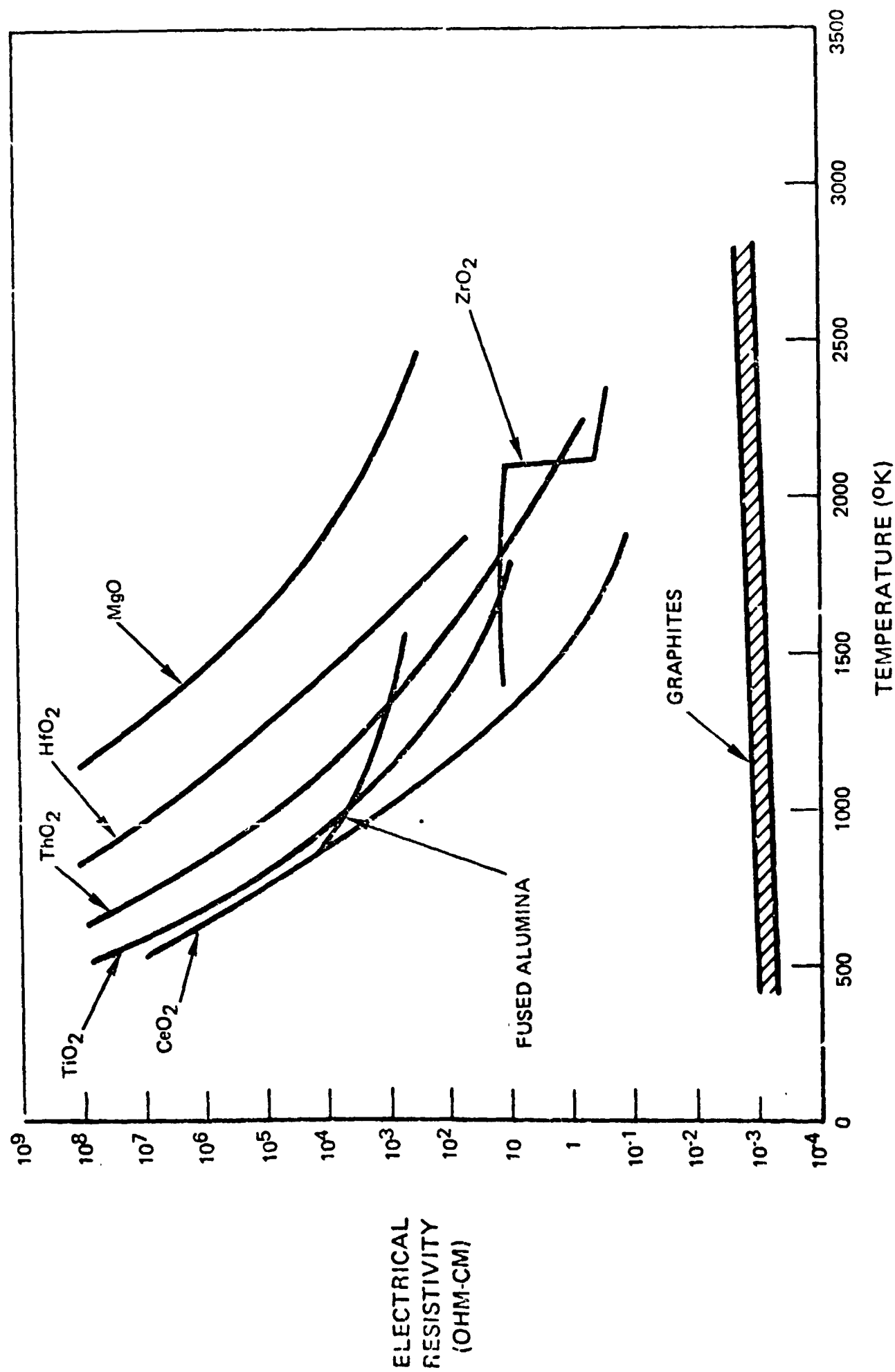


Figure 8

through 13 (borrowed from a NR/SD briefing to MSFC in 1970) show a concept for a space induction melting unit. The low efficiency of this process does not eliminate it from use. Should the power requirement for the experiment be well within that available in the space laboratory, then no serious problem exists. The use of a spherical reflector, for example, as shown in Figures 10 and 11 would reduce the power required to about one-third of that required with no reflector. Figures 10 and 11 show the use of a reflector in the melting and cooling cycles in association with induction coils. Figure 12 shows a schematic sketch of the over-all system visualized. Figure 13 shows schematically a system that would be required to cool the coils. Figure 14 shows the effect of the coil coupling efficiency on the power required to melt a one-half inch diameter sphere of alumina with and without a reflector. The use of a reflector does add some problems. First, it adds to the mechanical complexity of the system since it must be removed during the cooling cycle. It also significantly reduces visual observation of the melting. It will also need to be carefully designed so as not to "steal" power from the induction coils. While none of these problems are insurmountable they do exist and must be mentioned.

Figure 15 summarizes what is presently visualized as the steps required to induction melt in space. The reader is re-referred to Figure 7 for a summary of steps to be performed on the ground.

Reference is made to Appendix II for a discussion of power requirement calculations for induction melting and the power calculated to be required for melting typical unique glass compositions which have shown promise in our laser melting experiments. It must be borne in mind that the calculations are based on data which, in many cases was assumed. Therefore the numbers calculated are not to be taken as precise.

CONTAINERLESS MELTING & COOLING (PREHEATING)

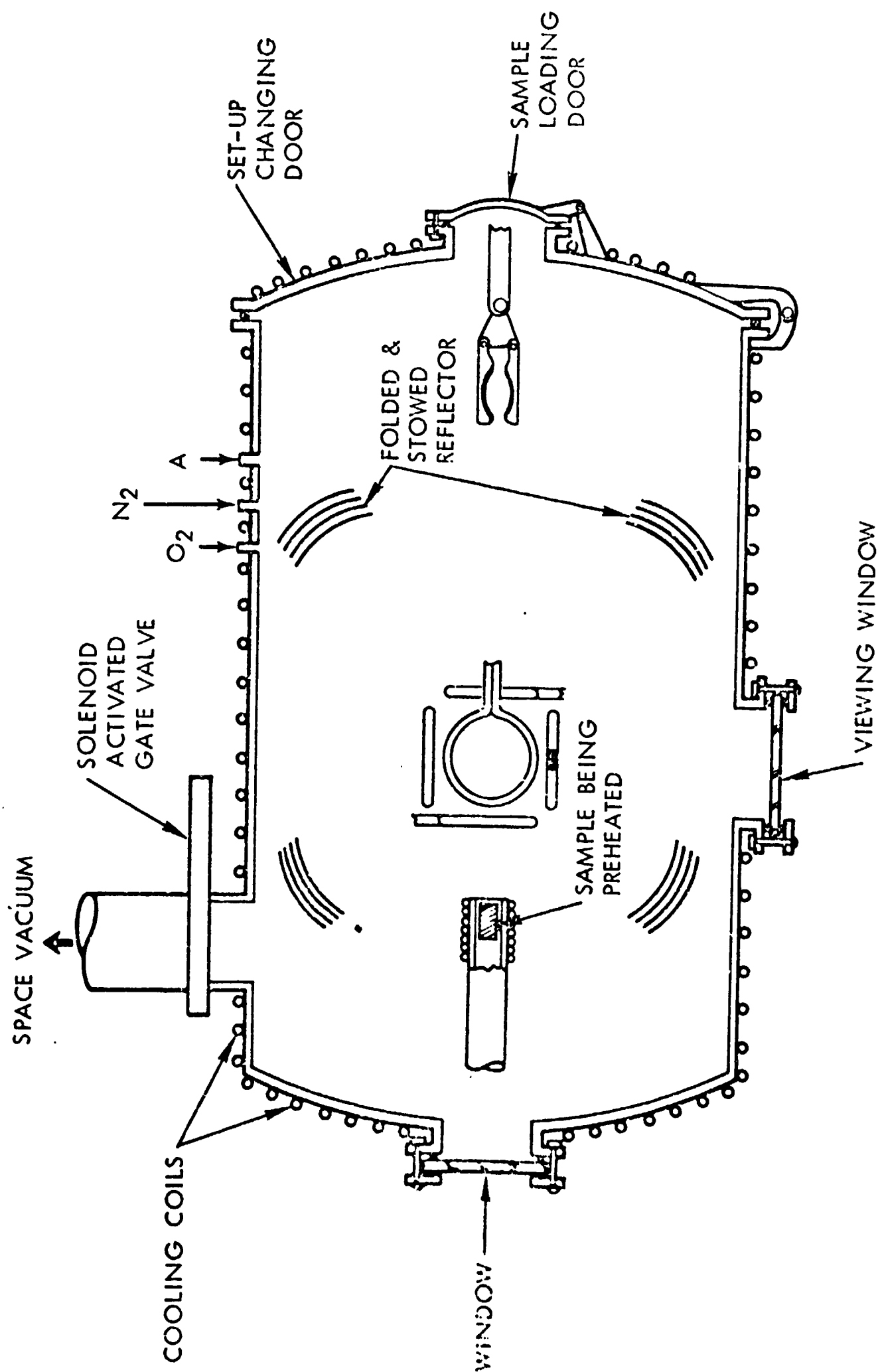


Figure 9

CONTAINERLESS MELTING & COOLING (MELTING)

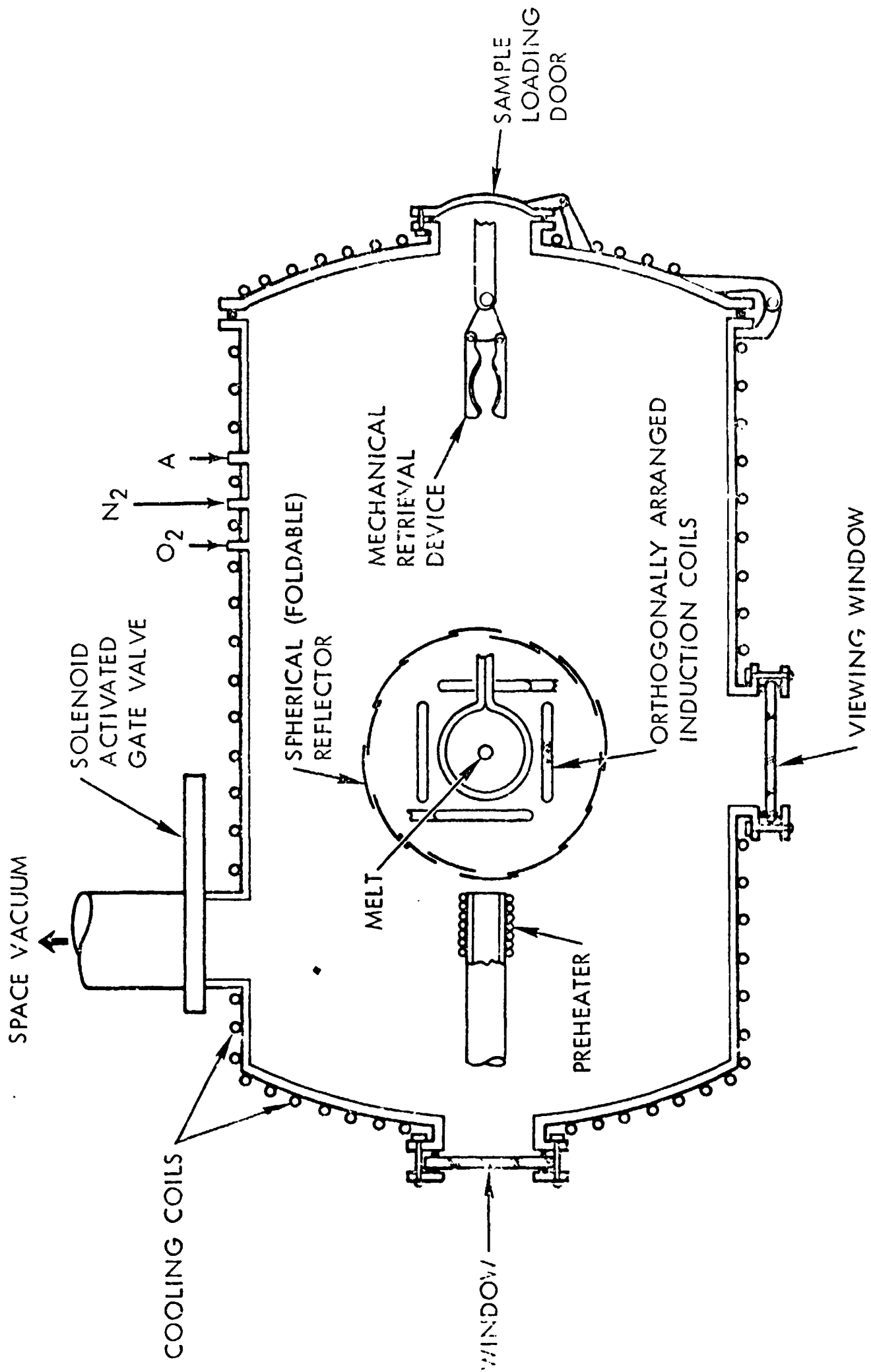


Figure 10

(COOLING)

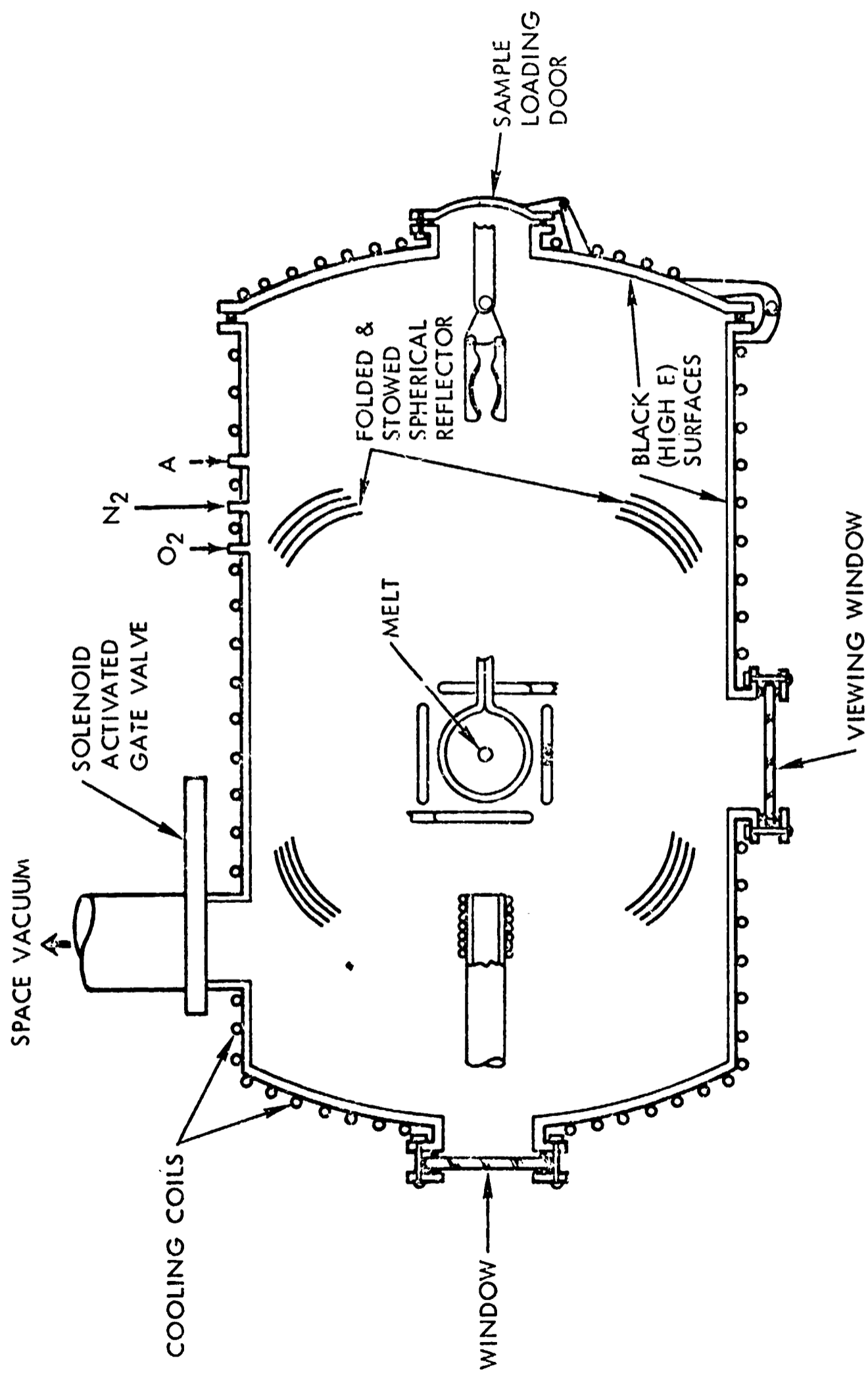


Figure 11

OVERALL SYSTEM SCHEMATIC

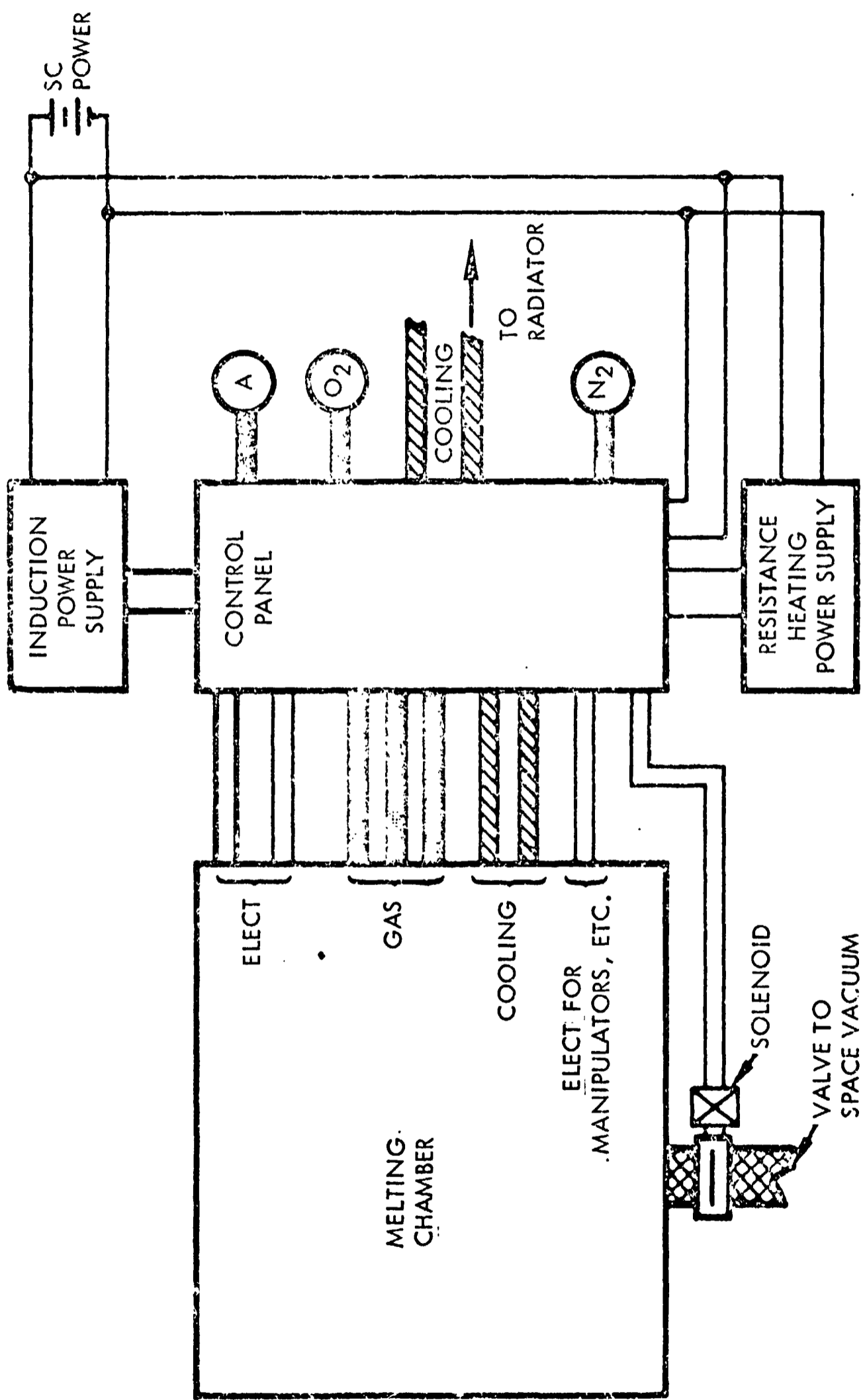


Figure 12

TEMPERATURE CONTROL SCHEMATIC

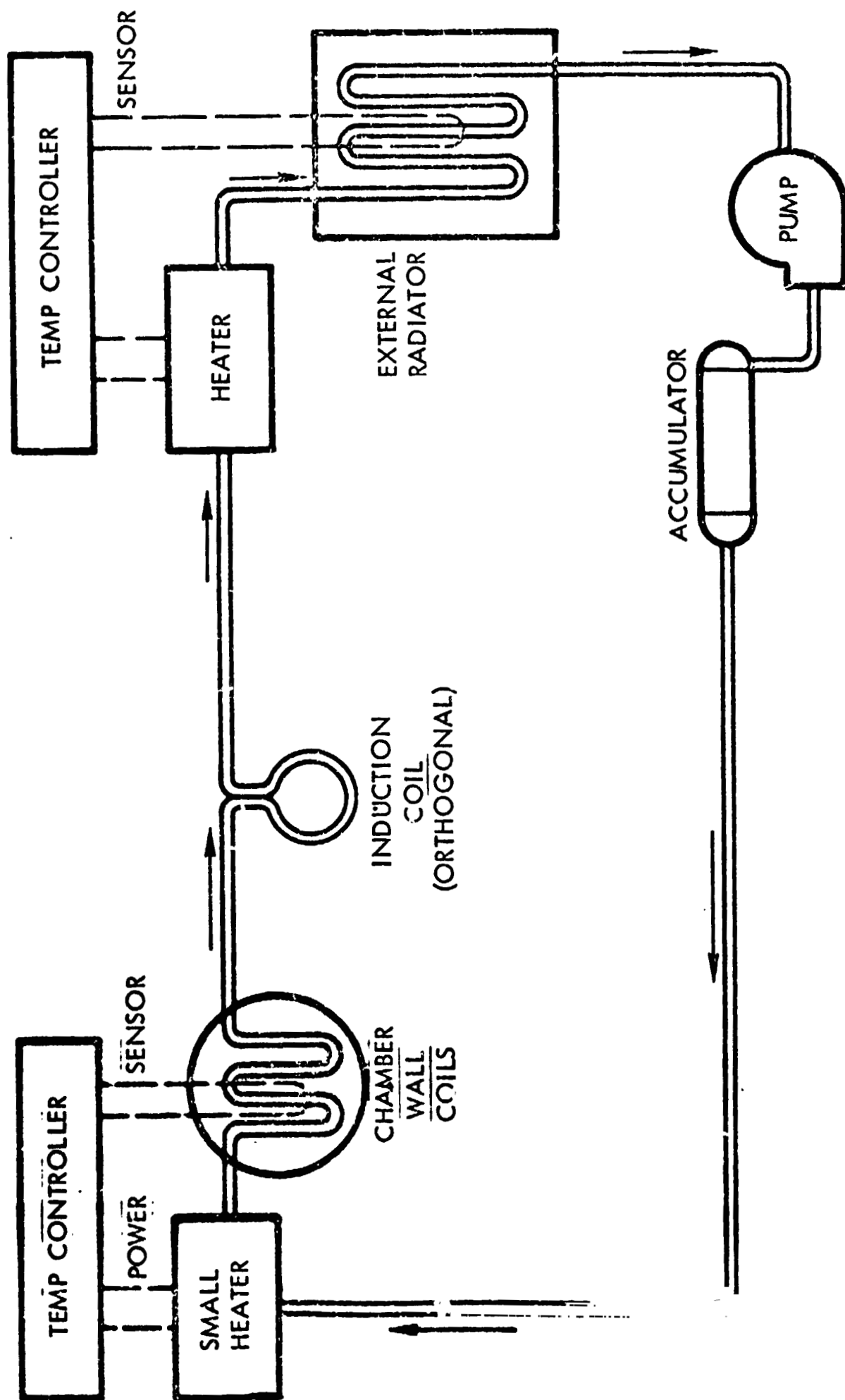


Figure 13

EFFECT OF COIL COUPLING EFFICIENCY ON POWER REQUIRED TO MELT 0.5-INCH DIAMETER SPHERES OF Al_2O_3

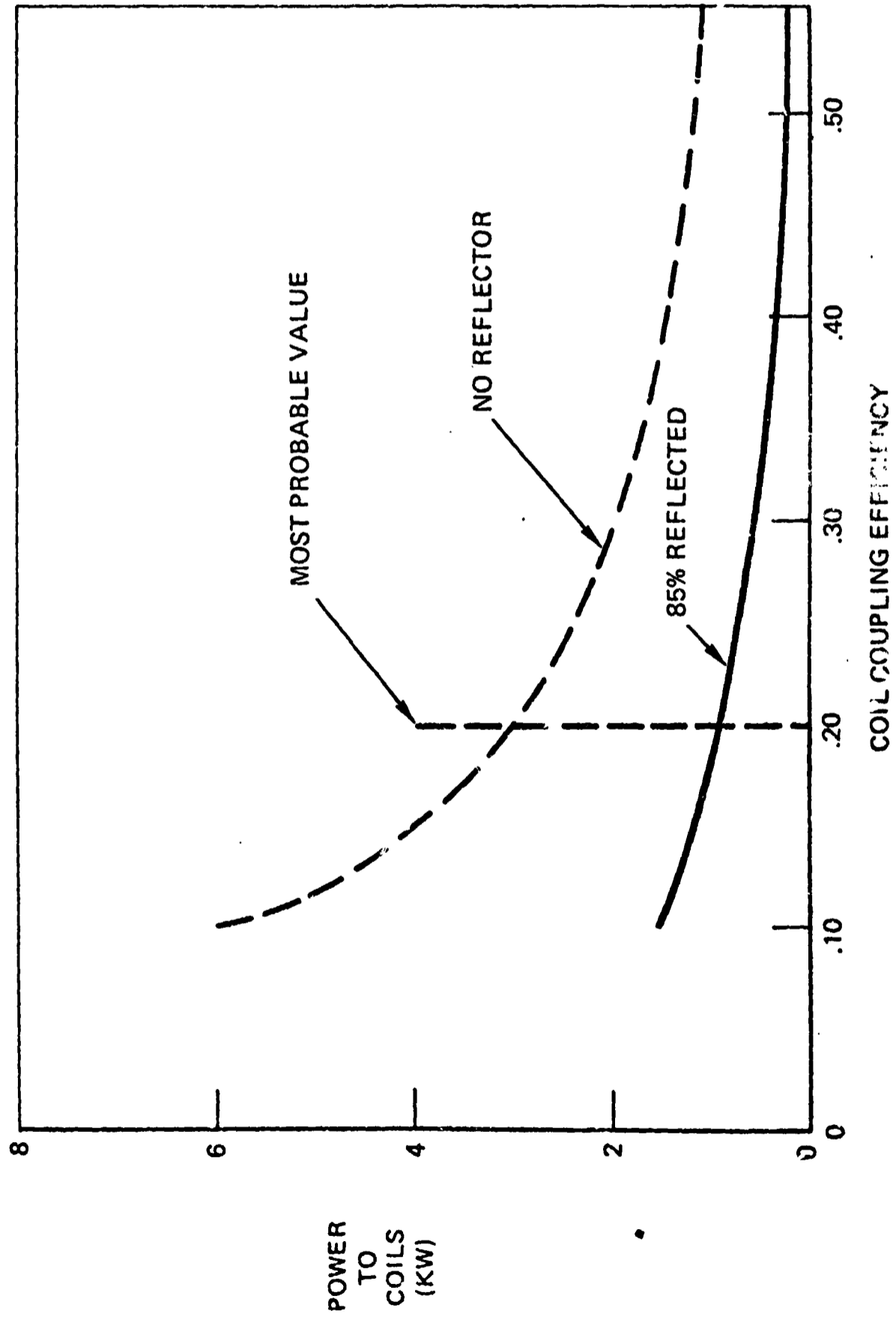


Figure 14

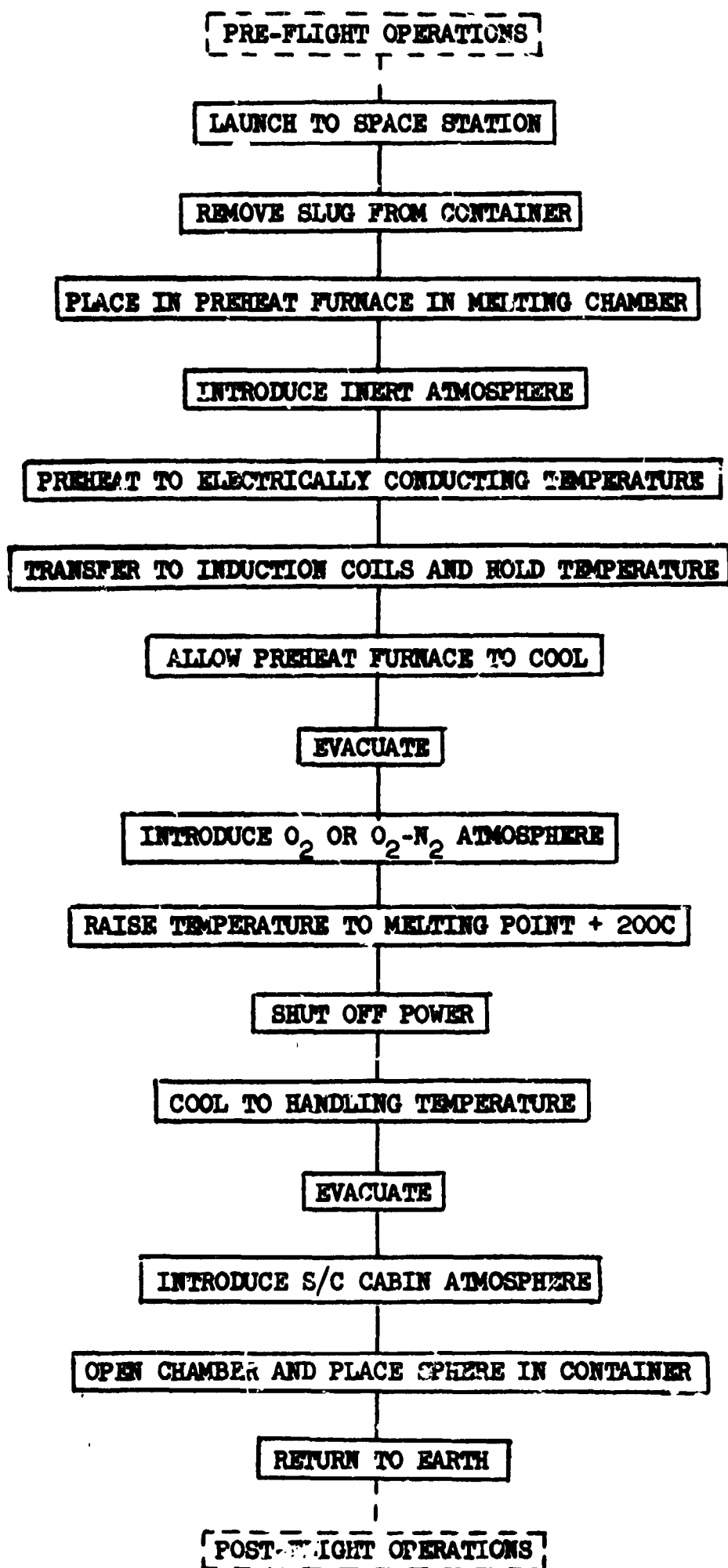


Figure 15 POSSIBLE FLIGHT OPERATIONS FLOW DIAGRAM - - INDUCTION MELTING

Laser

The CO₂ laser has already proved itself admirably for melting oxides. All of the work done to date on making small spherules of unusual glasses has utilized a continuous CO₂ laser as the heat source. Heat transfer from the beam, operating in the infrared at 10.6 microns, and the oxide material appears to be very efficient. No difficulty has been experienced in melting and superheating the many compositions melted to date.

The CO₂ continuous laser is a clean power source, can be operated in any foreseeable atmosphere, and does not require any return circuit, since heat transfer is optical—not electrical. It therefore appears to meet all of the requirements as set forth earlier in this section. A further advantage of the laser as compared with induction is that preheating is not required, the laser working very well from room temperature through melting and superheating. Figure 16 shows a possible flow diagram for laser melting in space. By heating the free end of a rod held in a mechanical feeding device, a large molten pool could be developed on the end of the rod in a "zero" gravity field. Since the hot end of the rod would become electrically conducting, as discussed earlier, the molten pool, after separation from the solid portion of the rod, could be held in place with an electromagnetic positioning device. Such a device would serve the purpose of centering the melt to overcome small G forces introduced by astronaut motions, orbital eccentricities, etc. It may be anticipated that the small propulsion effect of the laser beam would be easily counteracted by such a positioning device.

The laser shares a disadvantage with induction in that conversion efficiency is relatively low, less than 20% of the electrical energy fed into the unit being converted to heat in the beam. The remaining electrical energy generates heat in the power conversion equipment and in the CO₂ gas and must be removed

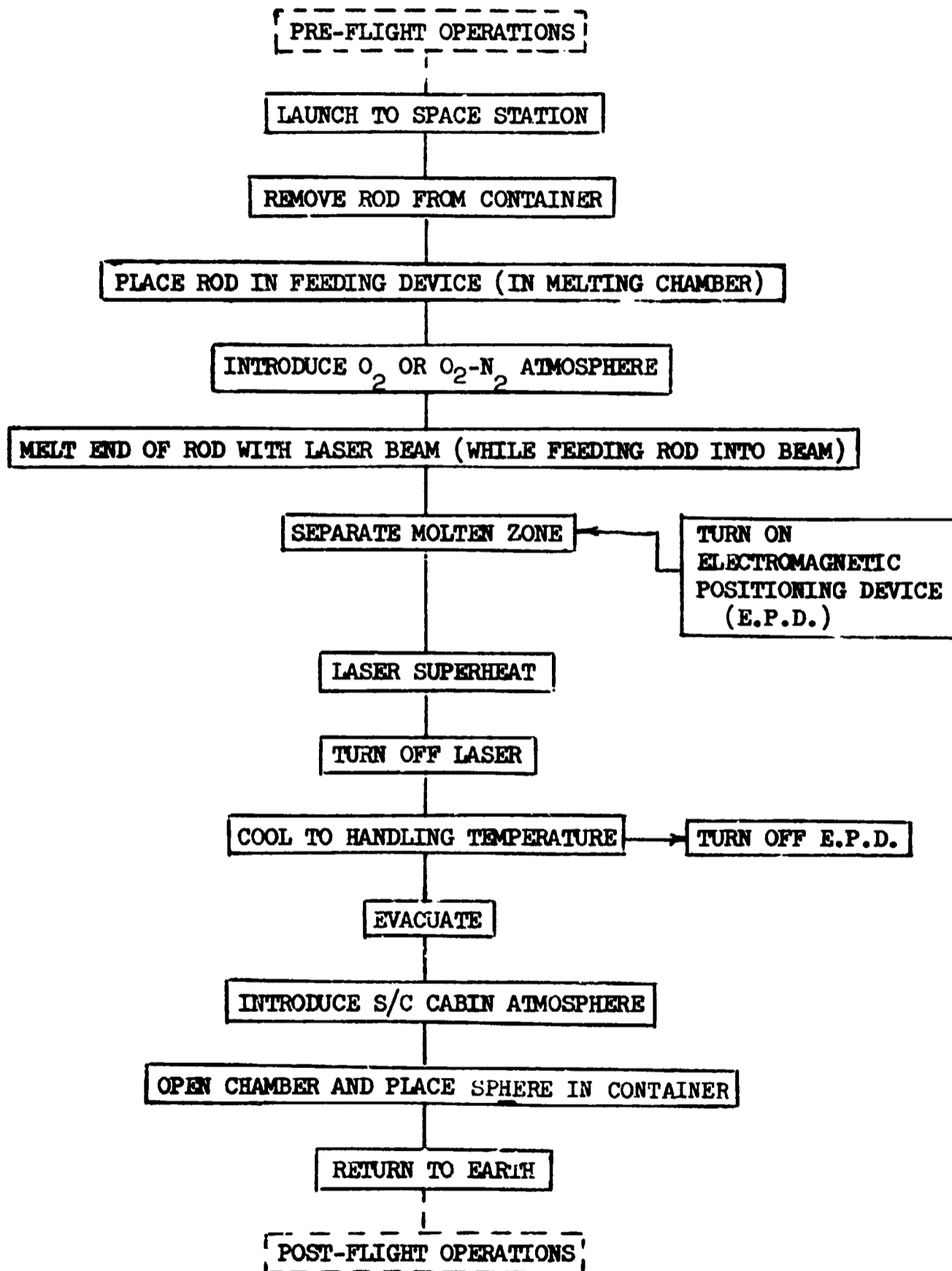


Figure 16 POSSIBLE FLIGHT OPERATIONS FLOW DIAGRAM - - LASER MELTING

by use of a cooling fluid. Thus a cooling system would be required similar to that shown schematically in Figure 13 for an induction set-up. In the laser case, the cooling coil would extract heat from the power converter and would also surround the CO₂-containing tubes in the laser unit and would replace the induction coil shown in Figure 13.

An intriguing possibility for the laser appears worthy of further study. An unfocussed laser beam is well collimated parallel light. This suggests the possibility of placing the laser beam generating equipment on the ground, possibly on a mountain top, and directing the unfocussed beam by means of a tracking mirror to the orbiting space station. A mirror aboard the station could receive the beam and direct it into the work area through an infrared-transparent window in the wall of the space station. Inside the station the beam could be run through focussing optics and used for melting the material. Attenuations of the beam through the atmosphere should be slight, the principal losses being scattering and beam divergence. Beam wiggling caused by atmospheric turbulence would possibly be a serious problem when the station was near the horizon. Even so, duty cycles of 15 minutes to 1/2 hour are foreseeable and would be adequate for the type of operations visualized.

Such an arrangement would require extremely accurate pointing and tracking and further study would be required in this area to determine feasibility. If such an arrangement can be worked out, weight savings should be very large. The only weight aboard the space station would be in the receiving and focussing optics and possibly in monitoring support equipment. The heavy transformers and cooling system would be located on the ground where electrical power is also not at a very great premium.

Resistance Furnace

The electrical resistance furnace does not appear at this writing to be a serious contender for melting oxides of interest. The principal problem is that the highest temperature resistance heating elements have maximum working temperatures that are far too low for most of the materials of interest. Silicon carbide and tungsten both have useful working temperatures below 1900C. In the case of tungsten an inert furnace atmosphere would have to be used. Resistance furnaces are logical for preheating and more will be said about them in a later portion of this section.

Electron Beam

It would appear that the electron beam could be developed into a useful power source. Problems that would have to be overcome include provision for adequate return circuits, possibly by providing targets behind the sample; and provision for an atmosphere. There appears to be serious question about the interaction of an electron beam with an electromagnetic positioning device. It would appear at this writing that, while none of the major problems foreseen are unsolvable, there is little incentive for developing electron beam equipment for glass melting - both laser and induction appear to pose less problems.

Solar

The use of a solar concentrator for direct melting was discussed in a talk given by the principal investigator at MSFC (1). Such a method appears to have considerable merit, especially when considering the melting of very large glass spheres, where electrical power generation in space in sufficient quantity may be a serious problem.

(1) Happe, R. A. "Possibilities for Producing New Glasses in Space"
ME-69-1, October, 1969

The use of a solar furnace in connection with experiments aboard a manned space laboratory does not appear feasible unless there is a willingness to orient the whole laboratory with the sun. If this could be done, an optical system could be devised to collect the concentrated solar energy and direct it into the work area. It might be possible to devise a system where the solar furnace only would point to the sun with an optical system to track the beam with respect to the laboratory and direct it into the work area. Another possibility would consist of a movable tracking mirror on the sun side of the solar concentrator. This latter would appear to be a bit simpler than the previous possibility. It was deemed outside of the scope of the present study to delve into detail but it would appear on the surface that all of them are pretty hairy. Until it can be established that a solar beam is capable of superheating a molten oxide pool, there appears to be little incentive for attempting to cope with the other problems. There is considerable question as to whether the molten glass would become transparent to the visible, solar energy with the result that once melting had been achieved there would be little or no energy transfer to the melt. Perhaps some simple experiments can be run in connection with other methods of heating during flight experiments to resolve this question. It should be possible to measure transmission by beaming sunlight through a molten sphere suspended in space provided the energy being given off by the hot sphere and the sunlight can be adequately separated.

Chemical

Flame heating must be considered low on the list of possible heating methods principally because of potential difficulty with contaminating the melt through reaction with combustion products. Disposal of voluminous combustion products does not appear to be a very simple matter either.

Thermit reactions share the disadvantage of gas flames in that the melt could be contaminated by combustion products, which would also have to be removed. Difficulty of controlling such reactions, both from an operational and from a safety standpoint discourage their serious consideration at this time.

Arc

Electrical arcs appear to be candidates for melting oxides although there is a possibility that heat transfer may be a problem for similar reasons that the use of solar energy is in question. All in all their use does not appear to be so attractive as laser and induction.

CHAMBERS

Design of the chamber and associated hardware configuration will have to consider the work area size, material selection and design criteria, experiment visibility, accessibility, experiment requirements, and tie-in requirements of power, gas, etc. Analogous considerations include the reuse criteria, i.e., will the chamber become contaminated during one melting operation to adversely affect a second experiment and if so, what can be done to clean the chamber? While it is almost a foregone conclusion that the chamber will have to be externally cooled, the actual degree of cooling may be process oriented. More specifically, if internal reflectors are needed to increase the efficiency of the heating zone, then a reduced cooling capacity may be required. On the other hand, if the walls of the chamber or supplemental internal fins (or flaps) are required to aid in cooling the superheated material to allow a reasonable cooling time or provide a minimum cooling rate for the formation of a glass, then an increase in cooling capacity would be needed.

PREHEATING

Some of the basic heating methods require preheating the materials in order to render them electrically conductive. Preheating appears to be essential for induction melting of oxides, since they are dielectrics at room temperature. In the event resistance heating develops as a preferred heating method for manned laboratory use based on sounding rocket experiments, preheating would also be required.

The preheating temperatures required, in the range 1100 to 1800C, appear within current state-of-the-art for electrical resistance furnaces. At the lower end of the range nichrome and kanthal wound furnaces can be used. In the intermediate portion of the range, platinum wound furnaces or furnaces with silicon carbide (globalar) elements can be used. For the upper part of the range molybdenum or tungsten wound furnaces can be employed. In such a case a protective atmosphere must be used because of the high oxidation rate of the refractory metals. The use of an atmosphere that is not optimum for the material being melted does not appear to pose a serious problem. The protective atmosphere can be quickly removed from the chamber utilizing the space vacuum and an oxidizing atmosphere quickly substituted after the preheater elements have cooled (a matter of seconds in a suitably designed furnace). The flow diagram of Figure 15 shows how this might be accomplished.

POSITION CONTROL

The basic reason for performing a glass melting experiment in space is to obtain a condition where a material can be melted without a container. In order to produce a unique glass boule (spheroid) of significant size, a zero gravity field must be used. Because of astronaut motions, orbital eccentricities, location of experiments of the center of gravity of the spacecraft, etc. a free floating object will not remain in the exact position

with respect to the rest of the spacecraft where originally placed. Unless all free floating operations can be performed in an extremely short time span, it appears likely that some form of position control will have to be employed. Such position control can take one of two general forms.

- 1) The free floating object can be moved with respect to the vehicle.
- 2) The vehicle can be moved with respect to the free floating object so as to maintain the relative position of the object in the vehicle.

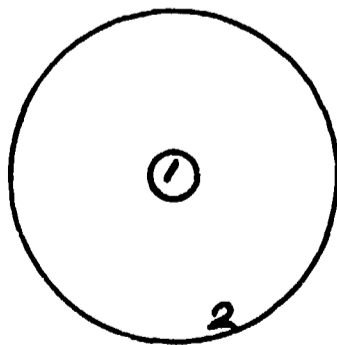
Considerable work has been done under NASA sponsorship on the use of electromagnetic devices for position control. This technique has the further advantage that it might be possible to counteract the propulsive effect of such heating sources as electron beam and laser beams. A small disadvantage of such a scheme is that it works only for electrically conductive materials. In such a case molten glass could be held satisfactorily but the position control would be lost on cooling after the material ceased to become electrically conductive (at temperatures below the 1800 to 1100C range). Since the cooling rates with radiation cooling are extremely high, as are the glass transition temperatures, this should not pose a serious problem with experimental sized glass spheres in the 1/2 - inch to one-inch diameter size class.

In the case of laser melting, it might prove advantageous to split the beam into three or four beams all converging on the sample from different, equal-angled directions. This might accomplish position control during melting and superheating by utilizing the propulsive force advantageously. During cooling the material, of course, would be free to float, unless the beams were left on at low power. Since the cooling times to the glass transition temperature for 1/2 - inch diameter glass spheres are under four seconds (see next section on cooling), it would appear that position control during cooling may not be necessary.

COOLING

Cooling is perhaps the easiest part of the process to define at this time. Because of the high melting points of the oxides of interest for glass making, radiation cooling should permit very high cooling rates, the rates being a function of temperature to the fourth power. In addition, since temperatures are high, where the radiated energy is largely in the visible portion of the spectrum (the samples are white hot) the transparency of the material works to advantage and radiation can occur from within the mass as well as from the surface.* Because of radiation conductivity it should be possible to achieve very high cooling rates throughout the mass of the glass spheroids with very small thermal gradients being present. This same phenomenon might enable materials with relatively large expansion coefficients to be rapidly cooled without setting up large thermal stresses with possible attendant cracking.

As noted earlier, the cooling time should be a significant factor in the evaluation of the type of position control needed especially when preparing larger boules in space. In order to obtain a feel for the time scales involved cooling rate, cooling rate calculations were performed as follows:
The model used was:



* For a discussion of "radiation conductivity" in glass, the reader is referred to "Glass Engineering Handbook" by E. B. Shand, McGraw-Hill, 1958. The discussion of radiation conductivity is contained on pages 27-30.

where,

1. is the melt at a temperature, T_1
2. is a spherical enclosure with blackened walls ($\epsilon = 0.9$) maintained at a temperature (T_2) of 200 F.

The formulas used in the calculations were:

$$(I) \quad q = \sigma F_e F_a A_1 (T_1^4 - T_2^4)$$

where,

q = rate of heat transfer from (1) to (2) in BTU/Hr

σ = Stefan-Boltzmann constant (= 0.173×10^{-2} BTU/ft² (°R)⁴.Hr.)

F_e = Emissivity factor (Eq.II)

F_a = Configuration Factor (=1)

A_1 = Surface area of (1) in ft²

T_1 = Temperature of (1) in °R

T_2 = Temperature of (2) in °R

$$(II) \quad F_e = \frac{1}{\frac{1}{\epsilon_1} + \frac{1}{\epsilon_2} - 1}$$

where,

ϵ_1 = Emissivity of surface 1.

ϵ_2 = Emissivity of surface 2.

$$(III) \quad \Delta t = \frac{3600 (\Delta T) CM}{q}$$

where,

Δt = time increment in sec.

ΔT = increment of temperature drop in °R

C = specific heat in BTU/lb.

M = mass in lbs.

q = heat transfer rate (from I) in BTU/hr.

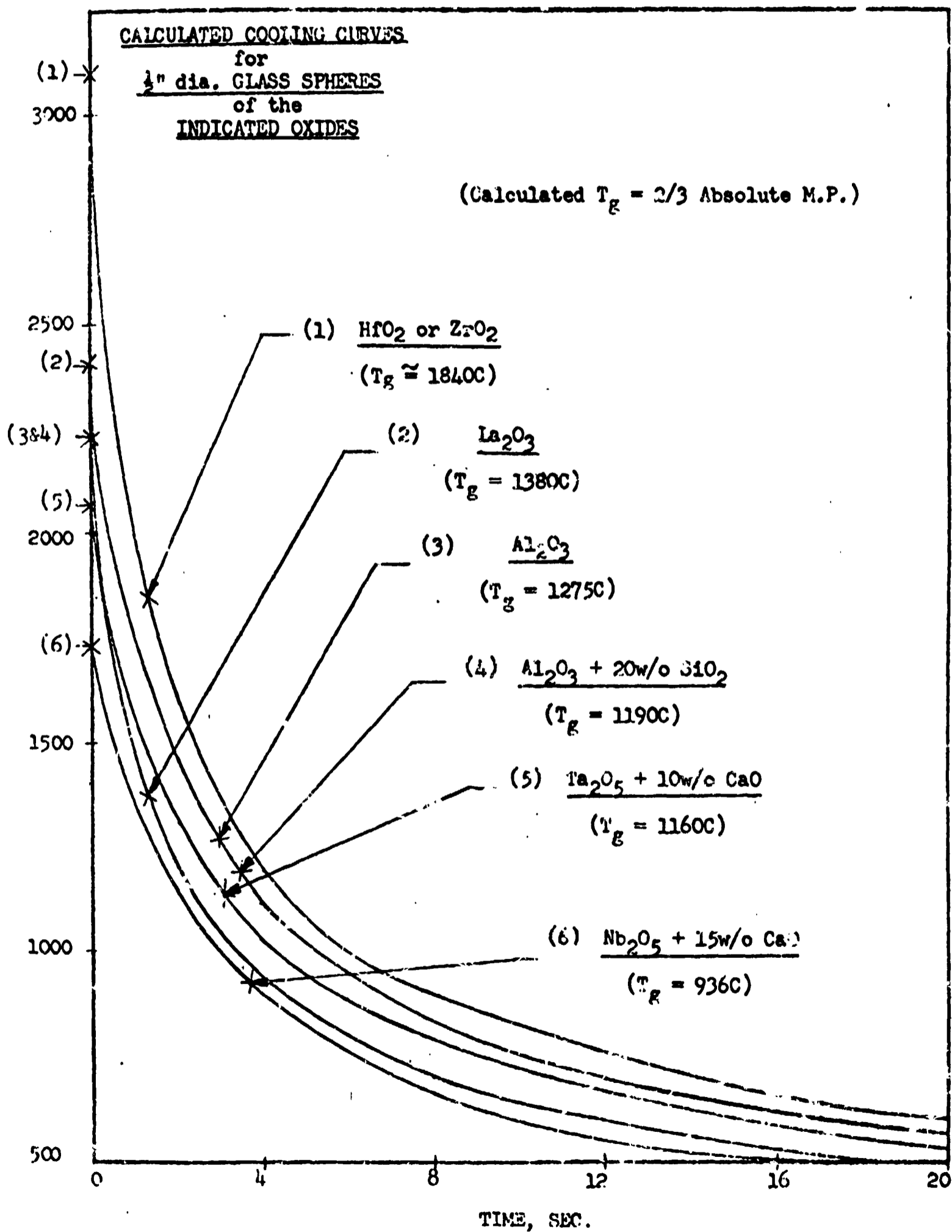
Assumed material property values are listed in the following table and in Table II-1 of Appendix II.

	<u>Al₂O₃</u>	<u>HfO₂</u>
Approximate Melting Point, °C	2050	2897
Superheat Temperature, °C	2250	3097
Density, lbs/ft ³	222	604
Specific Heat, BTU/lb·°F	0.31	0.12
Estimated Emissivity at Melting Point	0.5	0.5

Using equation I, q values were computed for (T_1) temperatures from 1000R to 7000R in 500° increments. A curve of q vs. T was plotted. Values of q for subsequent calculations were read from the q vs. T plot.

Using equation III, cooling time increments were calculated for 500°R temperature increments from the preheat temperature to well below the estimated glass transition temperature (T_g) for each oxide. The cooling time increments were cumulated and the cooling curves so obtained were plotted in Figure 17.

Cooling times to the glass transition temperature, where it is assumed that a glass will be sufficiently rigid to be handled: and to 600C, safely below the melting point of an aluminum handling fixture, are obtained from Figure 17 as follows:



<u>Material</u>	<u>Approximate Cooling Time, Sec., to:</u>	
	<u>Tg</u>	<u>600C</u>
HfO ₂	1.2	20
Al ₂ O ₃	2.6	17
Al ₂ O ₃ + 20 w/o SiO ₂	3.2	17
La ₂ O ₃	1.4	12
Ta ₂ O ₅ + 103/o CaO	3.0	15.6
Nb ₂ O ₅ + 15 w/o CaO	3.6	11

These calculations are approximations and do not account for the following:

- a) Emittances for the higher temperature materials at temperatures near their melting points have not generally been measured.
- b) Emittance and specific heat are not constant over the temperature range of interest.

It is probable, however that the above and other uncertainties should not cause the calculated results to be in error by more than about $\pm 50\%$.

It should also be noted that the calculations assume radiant heat transfer only. Errors introduced by neglecting other modes of heat transfer at the higher temperatures should be trivial. At the lower temperatures, where the bulk of the time is consumed, the more significant errors introduced by failing to consider conduction and convection should give calculated cooling rates lower than will be actually experienced unless the surrounding atmosphere is a vacuum. Therefore the calculated results may be considered conservative.

It should be stressed that the rates calculated, within the limits of the errors considered above, represent the maximum rates achievable in containerless melting space experiments. In the case of glass experiments it will generally be desirable to utilize the maximum rate of cooling possible. The cooling

rates can be reduced, if necessary, by "bucking" with power during the cooling cycle. If induction or the multiple laser beam concept is used for heating, the application of power should also result in a restorative force tending to prevent drifting of the melt.

There is a simple method for calculating cooling times for diameters other than one-half inch. Since the mass of the melt is a function of the cube of the diameter and the surface area a function of the square of the diameter, changing the diameter by a given factor should change the cooling time by the same factor. For example, doubling the diameter of the melt should result in a doubling of the cooling time.

Because the cooling curves approach the temperature of the chamber asymptotically, the simplest way of reducing the time for cooling is to raise the temperature at which the sample is mechanically grabbed. It is apparent from the curves of Figure 11 that the differences in melting points have only a small effect on the cooling time because all of the cooling rates are extremely rapid at the higher temperatures.

"CONVENTIONAL" GLASSES IN ZERO GRAVITY

Dr. E. Deeg of the American Optical Corp. was contacted to determine a fruitful area of research for employing zero gravity to improve the quality of large pieces of optical glasses presently prepared with limited success under terrestrial conditions. Two classes of glasses subject to micro-phase separation and demutification under one G conditions, presumably caused by the density difference between the micro-phase and the parent glass have been identified. Specific compositions representing extreme cases suggested by Dr. Deeg are given in Table V. One class of such glasses is the fluor-crown and phospho-fluor-crown glasses, compositions A, B, E, and F of Table V. Another class is high titania content glasses, compositions C and D of Table V.

Consideration has been given to preparing such glasses using the laser melting and free-fall cooling technique employed for the unique glasses. It has been concluded that the chances of successfully preparing such complex glasses by starting with mixed oxide rods and laser melting appear poor. Two considerations appear to counter-indicate such a technique.

- 1) The compositions are quite complex there being a minimum of five constituents and a maximum of ten. It is felt that there would be considerable difficulty obtaining homogeneous glasses using such techniques.

- 2) The melting and boiling points of some of the major constituents are quite low. This could lead to significant composition shifts during melting, where the low-boiling constituent would be vaporized

before it could be put into solution. Particularly troublesome in this regard are the oxides, P_2O_5 , B_2O_3 , Li_2O , Na_2O , K_2O and possibly the fluorides, AlF_3 and the acid fluoride KHF_2 , the latter subject to decomposition at a low temperature.

A better way of handling such glasses would be to prepare them by conventional terrestrial melting techniques in the form of rods. Depending on their size, these rods might be remelted using the laser free-fall technique or, alternatively, the ends of the rods could be torch-melted and the drops so formed allowed to free-fall cool. Viscosity and reboiling of such glasses might present serious problems, especially in spin-melting. If such turns out to be the case, it might prove more advantageous to postpone further experimental work for actual flight experiments.

Table V
Batch Compositions for Zero G Melting Experiments

	A	B	C	D	E	F
P ₂ O ₅	-	-	-	-	0.7	64.3
SiO ₂	52.0	48.3	57.0	40.5	69.0	8.0
TiO ₂	-	-	20.0	16.7	5.0	-
B ₂ O ₃	18.3	13.5	4.5	4.5	-	3.5
Al ₂ O ₃	7.8	-	-	2.0	18.0	14.8
As ₂ O ₃	0.2	0.3	0.5	-	0.7	0.6
Sb ₂ O ₃	-	-	-	4.0	-	-
MgO	-	-	-	-	2.5	0.1
CaO	-	-	-	-	-	4.9
BaO	-	-	-	-	-	-
ZnO	-	-	-	-	0.5	-
PbO	-	-	-	12.5	-	-
Li ₂ O	-	-	-	-	2.6	-
Na ₂ O	-	-	9.0	0.5	0.7	-
K ₂ O	7.3	-	9.0	8.0	0.1	-
AlF ₃	-	5.4	-	-	-	-
KHF ₂	14.4	32.5	-	12.0	-	0.8
Fe (metal)	-	-	-	-	-	1.5
Sugar	-	-	-	-	-	1.5

All compositions are in weight percent.

FUTURE WORK PLAN

As a part of the contract requirements, a study has been made of the future work required leading to the ultimate production of glasses, both new and "conventional" in space. Accordingly, a master plan has been developed tying in the needed steps with the latest NASA scheduling for Shuttle Sortie Missions and Space Station Missions. The discussion which follows is divided into two major sections: 1) The Master Plan and 2) Work Recommended During NASA FY 73, beginning in calendar July, 1972. The numbers in parentheses following each subsection correspond to the numbering system of the Master Plan Schedule (Figure 18).

MASTER PLAN

The Master Plan is shown in Figure 18. For purposes of convenience and logical development, there are two major subdivisions - I. Development Work Leading to the Production of Optical Glasses for Use in the Visible Spectrum, and II. Development Work Leading to the Production of Glasses for Applications Other than in the Visible Spectrum. The first would include such applications as lenses, windows, etc., all for the visible portion of the spectrum. The second subdivision, for example, would include such items as high temperature glasses and glasses for better transmission in the ultraviolet and the infrared portions of the spectrum. Specific possibilities include the following:

(a) New Superconductors of High Critical Transition Temperatures.

Amorphous superconductors like Pb, Bi, etc. in thin film forms have higher critical temperatures than corresponding bulk crystals. Liquid-quenched glassy superconductors have not been made. Space melting opens up possibilities of bulk samples of new glassy superconductors of high critical transition temperatures.

(b) New Hard Glasses

There are at least two important implications. (i) Hardness plus high refractive index gives potential "gem stone" quality glass.

(ii) Hardness means scratch resistance, in turn means high strength. Recent work done at UCLA indicates that if crystallization is suppressed, many glasses can be made with very high hardness values. Some such glasses contain BeO.

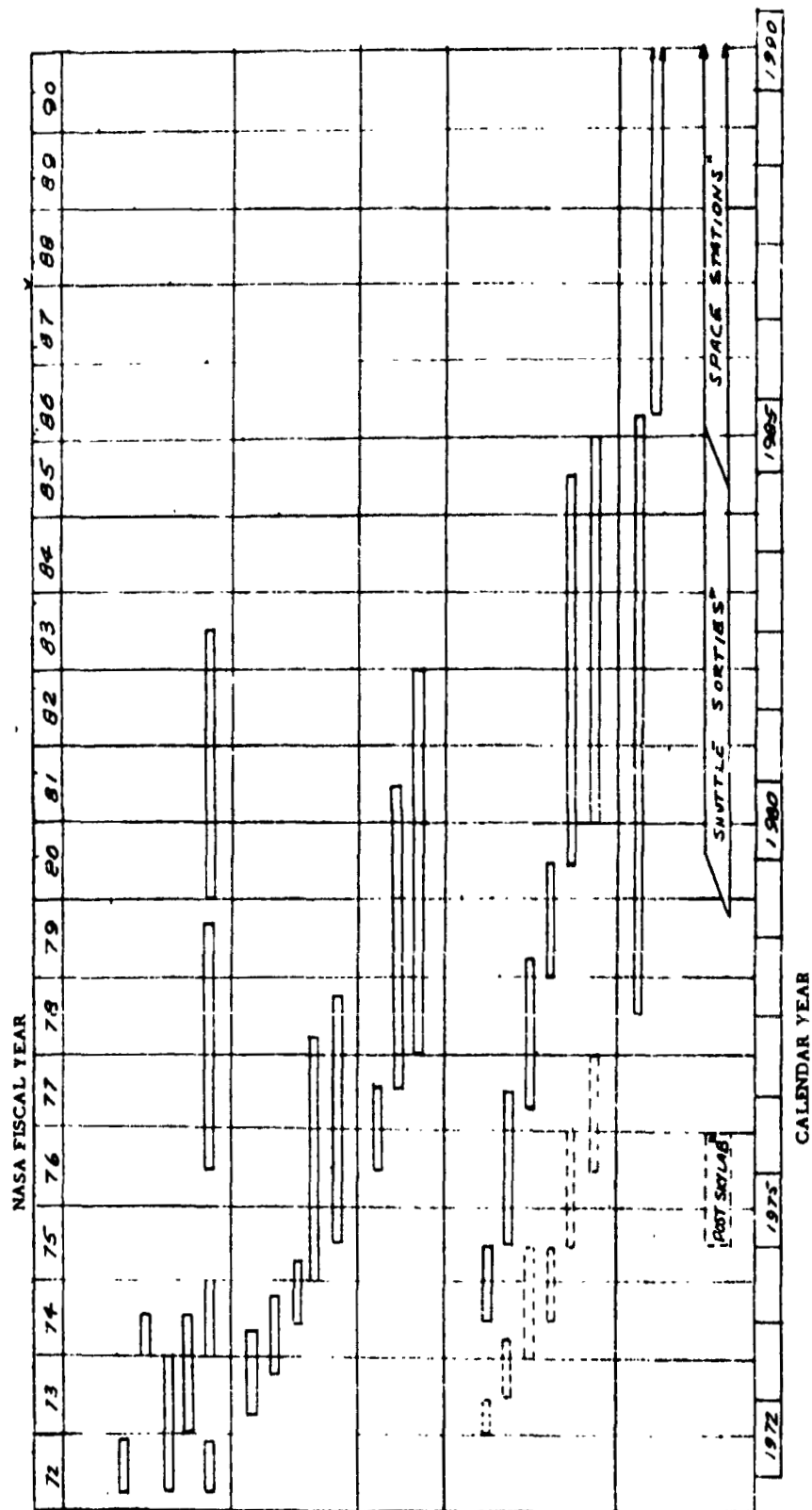
(c) New Glass Ceramics

Controlled crystallization of glass can yield transparent ceramics. Materials such as titanates and niobates, if prepared in transparent state, have important application possibilities in electro-optical devices. Such systems are not readily formed in a glassy state.. Space formation of such glasses and subsequent controlled crystallization can therefore yield valuable electronic materials.

For further examples, the reader is referred to Appendix I.

The scheduled dates shown for the Post Skylab, Shuttle Sortie, and Space Station missions were obtained from NASA HQ MT 71-5611 as revised on 1/25/72. The scheduling shown in Figure 18 was obtained by working backwards from these dates, assigning reasonable times for each step.

It is apparent from the Master Plan Schedule that most of the work needing to be done in NASA FY 73 falls into the areas of the Pre-Experiment Definition Studies (IA) and the Sounding Rocket Experiments (IB). In the event



- A. PRE-EXPT. DEFINITION STUDIES**
1. Flight Equipment Definition
 - a. Studies
 - b. Specifications
 2. Small Spherule (to 50 mil) Expts.
 3. Larger Spheroid Expts (to 1/4")
 4. Applications Studies
- B. SOUNDING ROCKET EXPERIMENTS - I**
1. Pre-Engineering Studies
 2. 1 pt. Package Design & Engineering
 3. " " Construction & Check Out
 4. Flight Expts. (1/2" dia. spheroids)
 5. Post-Flight Evaluation
- C. SOUNDING ROCKET EXPERIMENTS - II**
1. Expt. Package Des., Eng., Constr., Check
 2. Flight Experiments (> 1/2" Spheroids)
 3. Post-Flight Evaluation
- D. MANNED LAB EXPTS/DEMONSTRATIONS**
(Post Skylab, Shuttle Sorties, Space Stations)
1. Pre-Engineering Equipment Studies
 2. Equipment Design and Engineering
 3. Equipment Constr. & Check Out
 4. Operator Training
 5. Flight Experiment Operations
 6. Post-Flight Evaluation
- E. SPACE MANUFACTURING**
1. Pre-Operations Preparation
 2. Manufacturing Operations

* Per NASA HQ MT 71-5611 (Rev. 1/25/72)

Figure 18A. Master Plan Schedule -- I. Optical Glasses for the Visible Spectrum

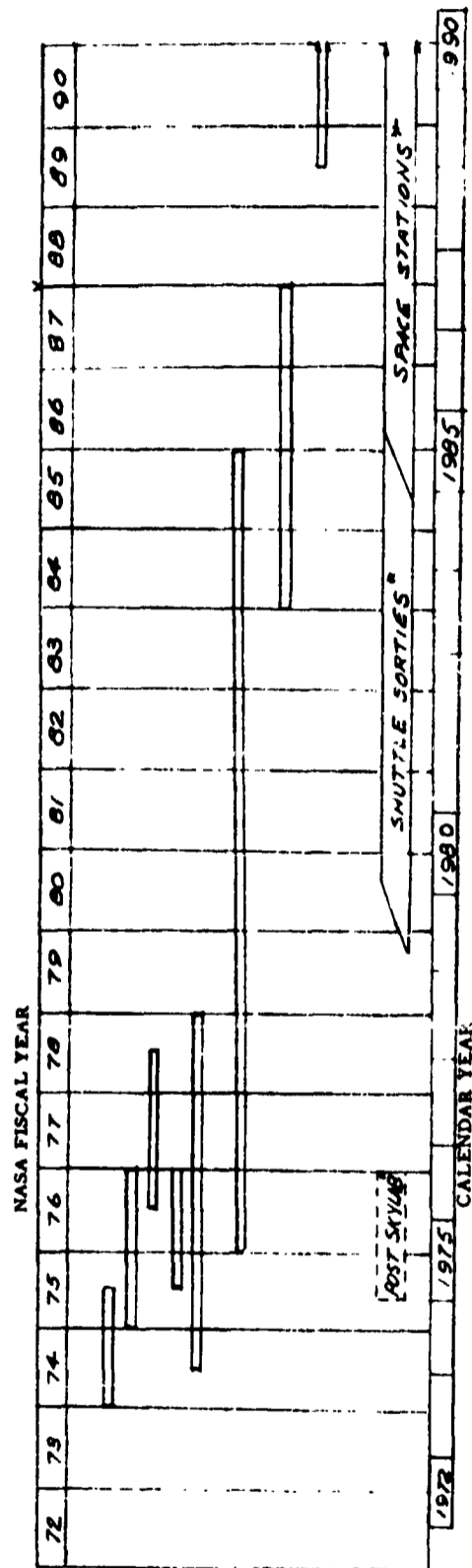


Figure 18R. Master Plan Schedule -- II. Glasses for Applications Other Than the Visible Spectrum

* Per NASA HQ MT 71-5611 (Rev. 1/25/72)

a Post Skylab mission is decided firmly by NASA and a glass experiment is indicated, then, of course, work leading to meaningful glass experiments for the Post Skylab should also be begun in FY 73. These latter events are shown dashed in the Master Plan Schedule because of the uncertainty at this time of those particular missions occurring.

A preliminary study has been performed of the feasibility of including meaningful glass experiments in the sounding rocket program. The conclusion of this study is that it indeed appears feasible using a resistance heating method of melting the oxide compositions. It is outside the scope of the present discussion to go into detail on this particular concept. However, a separate briefing is being prepared at this writing and will be presented to NASA-MSFC in the near future. This briefing will show how the resistance heating approach might be used for sounding rocket experiments and outlines development work needed to transform the concept into an operational reality. It is felt at this time that new glass spheres in the 1/2-inch diameter class might be successfully produced in the first generation of sounding rocket experiments. It also appears to be a distinct possibility at this time that larger sized glass spheroids might be producible in sounding rocket experiments as a second generation effort. There is one possibly significant disadvantage to the sounding rocket approach as compared with the manned laboratory approach, and that is that the resistance heating concept does involve superheating the molten material in contact with the crystalline, solid material. This would theoretically limit the number of compositions where one might expect to obtain glasses. Such

compositions would probably be limited to those which are better glass formers, the advantage of zero gravity production being principally the ability to melt them in the absence of a solid container - unobtainable because of the high melting points of the substances involved. It should be possible to containerless cool the materials in the sounding rocket experiments provided that a suitable method for separating the molten from the solid material can be worked out. If it cannot, a further restriction is placed on the number of glass forming materials possible.

Included in the time span allotted for the sounding rocket flight experiments in the Master Plan Schedule is pre-experiment sample preparation, i.e., the preparation of the ceramic rods that will be melted in the flight experiments, debugging flights, and glass spheroid preparation flights.

It is felt that most of the activities shown in Figure 1.7 are essentially either self-explanatory or their execution is sufficiently far into the future as to not require further explanations at this time. There are pertinent comments that should be made at this time regarding post-flight evaluations.

Post Flight Evaluations (IB5, IC3, ID6)

The study by the Perkin-Elmer Corporation (see Appendix I) has delineated important properties or characteristics that might be measured or evaluated as part of the post-flight evaluation phases of items IB5, IC 3, and ID6.

The larger sizes (i.e., hopefully 1/2-inch diameter or greater) of the spheroids obtainable during the sounding rocket and manned missions permits the precision measurements of the index of refraction, n , and the Abbe number, ν . This is important since many of the applications for the new space-produced glasses depend on an accurate knowledge of the partial dispersion, P . In order to obtain a meaningful P value, index of refraction measurements accurate to at least six digits to the right of the decimal are needed at several wavelength of light. A 1/2-inch diameter permits the cutting and figuring of suitable prisms whose index at various wave lengths can

be measured using a precision refractometer available at the Perkin-Elmer Corporation. This refractometer is a duplicate of a similar one constructed by the National Bureau of Standards.

In addition, the larger sizes of the spheroids obtainable during the flight missions permits the accurate determination of transmission characteristics, thermal expansion coefficient, α , modulus of elasticity, thermal stability (dn/dT and da/dT), figuring characteristics and abrasion resistance. The quality of glass produced in terms of residual strain, striae, and other qualities can also be assessed.

WORK RECOMMENDED DURING NASA FY 73

In accordance with the Master Plan Schedule, there are three major areas of work required during NASA FY 73: (1) Continuation of pre-experiment definition studies, (2) Beginning of pre-experiment studies for sounding rocket experiments, and, later in the year, beginning of experiment package design and construction; and (3) Beginning of pre-engineering equipment studies and equipment design and engineering for Post Skylab missions.

Pre-Experiment Definition Studies (IA)

Flight Equipment Definition (IA1). It is recommended that the flight experiment definition studies (IA1a) leading to equipment for the manned laboratories not be continued in the present form during FY 73. Such studies leading to equipment for the Shuttle Sortie Missions can logically be delayed until mid-FY 74, based on present Shuttle Sortie schedules. More specific work should be begun for the sounding rocket shots and will be discussed in a later section as part of the sounding rocket experiment program. In the event the Post Skylab program materializes, an accelerated program for equipment designed to do a satisfactory job with glass must be begun in FY 73 as a logical part of that program. In FY 74 preliminary specifications (IA1b) should be prepared to guide the development efforts for the Shuttle Sortie

missions. These specifications should be prepared based on information obtained during the FY 72 and 73 experimental programs.

Small Spherule Experiments (IA2). Work begun in FY 72 under the present contract should be continued in FY 73. This work utilizes laser melting a spinning ceramic rod and free-fall cooling the droplets formed. It is a useful and economical technique for screening suitable compositions for subsequent, large scale experiments. Types of new compositions that might be investigated include:

a) New systems not previously tested, such as TiO_2 -CaO and some of the rare earth oxides (lanthanides).

b) Mixtures of systems whose components have given promising results.

Initial work should concentrate on binary mixtures with and without addition agents such as SiO_2 and CaO. Some of the binary systems that might be investigated include:

La_2O_3 with Al_2O_3 , Ga_2O_3 , Nb_2O_5 , Ta_2O_5 , Y_2O_3 , Sm_2O_3 , and Gd_2O_3 ; Nb_2O_5 with Al_2O_3 and Ga_2O_3 ; Ta_2O_5 with Al_2O_3 and Ga_2O_3 ; Y_2O_3 with Sm_2O_3 , Gd_2O_3 , Al_2O_3 , and Ga_2O_3 .

c) High melting non-oxide substances, such as ZnS (sphalerite), ZnSe, SnTe, CdSe, and PbTe.

The optical properties measurements; i.e., refractive index, n , and Abbe number, V , should be continued and should include all the glasses obtained during the FY 72 (present) program and the new ones obtained during FY 73.

Samples of the glassy spherules produced should be analyzed to determine composition and to ascertain that the compositions of the ceramic starting rods were not altered during laser melting.

In the event satisfactory arrangements can be made with an optical glass producer to prepare starting rods of selected "conventional" glass compositions and to evaluate spherules prepared by NR for micro-phase separation (See earlier section of this report on Conventional Glasses), small spherules will be produced by the laser spin casting technique. Because of the complexity of these compositions and the amount of low boiling point constituents, it is felt that they would not lend themselves to laser melting of pre-pressed ceramic rods.

Larger Spheroid Experiments (IA3) Attempts should be made to produce larger spheroids, in the 1/4-inch diameter class. The CO₂ laser on hand at the Space Division has enough power to melt and superheat a sufficiently large sized pool on the end of a rod. The starting rod could be mounted vertically and rotated slowly, and the laser beam could be directed horizontally. Initial experiments might entail melting large drops from rods of selected compositions which formed good yields of glass spherules in the screening experiments and allowing them to drop a short distance (approximately seven feet) into water.

Those compositions which yielded glasses in the initial, short-free-fall tests could be retested in a 100 foot drop tower available at the Space Division. The portable 250 watt laser unit, presently being used, could be installed in the top of the drop tower at the 80 foot level. An alternative arrangement being considered is to beam the unfocused parallel beam through a hole in the roof of the manufacturing building where it is now installed. The beam could be directed by a mirror to the top of the drop tower where another system of mirrors would bring it into position through the existing focusing optics (moved to the top of the drop tower).

The properties of the spheroids produced in the drop tower should be measured and the chemical compositions of all glasses should be analyzed.

Application Studies (IA4) Further applications studies are not recommended during FY 73. It is felt that until more data are available from larger spheroids, and further studies of the possibilities for producing glasses for applications in other than the visible spectrum (Item IIA1) are completed, the practical limit of what can be gained from applications studies has already been achieved as reported in Appendix I.

Sounding Rocket Experiments (IB)

A general description of the sounding rocket program is given in the previous Master Plan section. During FY 73, it is proposed that an accelerated program be begun. The initial effort would consist of pre-engineering studies. If such studies prove successful, experiment package design and engineering could be begun toward the end of the year.

The pre-engineering studies (IB1) would consist largely of experimental work to obtain empirical information for basing the design and engineering effort. Anticipated work in the pre-engineering studies would include:

a) Selection of Compositions. Compositions would be selected on the basis of glass formation tendencies as established in the Pre-experiment Definition Studies of IA. Further experimental work would be performed to establish the effects, if any, of melting in an inert atmosphere, such as Argon. Additional experiments would be performed on rods of suitable composition to establish preheating temperatures and suitability for resistance melting.

b) Determination of Resistance Heating Parameters. In an extension of the above tests on selected compositions, rods would be resistance heated to incipient melting and parameters such as electrical resistance, power inputs vs. temperature, and melting point measured. These data could be extrapolated through the melting point and to superheat temperatures about 400C* in excess of the melting point.

c) Evaluation of Separation Concepts. In order to separate the molten zone from the solid ends of the test bars, it will be necessary to "cut" the liquid at two planes in the flight experiments. Various approaches for doing this can be

* Because the resistance heating method involves liquid in contact with the crystalline solid, it is felt that the superheat temperature should be at least doubled that considered adequate for methods where the molten mass is isolated, as discussed elsewhere in this report.

evaluated terrestrially using laser-melted liquid drops on the ends of vertical rods. Candidate methods for "cutting" the liquid include gas jets, metallic or ceramic "scissors" and electrical vaporization. The amount of side motion imparted by each method evaluated will also be measured along with comparative estimates of cooling effects of the cutting methods.

d) Preliminary Study of Experiment -Rocket Interface. A non-experimental study of such factors as drift rates of the separated molten spheres, rocket attitudes at different portions of the flight, spin rates and affect on sample drift during cooling, etc., will be performed. During this study decisions will be reached concerning, for example, whether the rocket must be de-spun, whether an attitude control system must be used, or the experiment package only despun. This portion of the study will also be concerned with battery arrangements and preliminary electrical and timing circuitry to the extent that weights may be estimated.

Equipment for Post Skylab Missions (IC)

In the event that both (a) NASA firms a decision on Post Skylab and (b) a glass experiment will be included, an accelerated program must be begun to define equipment approaches and begin design and engineering. The initial work will consist largely of deciding whether to use induction or laser for melting and superheating.

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APPENDIX I

ENGINEERING REPORT NO. 10952

APPLICATIONS FOR NEW GLASS TYPES PRODUCED
BY ZERO GRAVITY FABRICATION TECHNIQUES

DATE: 15 FEBRUARY 1972

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ABSTRACT

The Space Division of North American Rockwell Corporation has recently proposed a new glass fabrication process which involves producing the glasses in a zero gravity environment.^{1A} This zero gravity melting eliminates the need for a solid container during both the melting and cooling phases of glass production. The combination of superheating well above the melting temperature and cooling in the absence of most normal nucleation sites suggests the possibility of producing glasses from normally crystalline materials such as Al_2O_3 , HfO_2 , ZrO_2 , etc. This report explores the possible applications suitable for such new glass types.

1A Happe, R., Journal of Non-Crystalline Solids, 3, 375-392 (1970)

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TABLE OF CONTENTS

<u>SECTION</u>	<u>TITLE</u>	<u>PAGE</u>
1.0	SUMMARY	1
2.0	INTRODUCTION	3
3.0	MATERIALS	4
3.1	GENERAL LIMITATIONS	4
3.2	SPECIFIC PROPERTIES	8
4.0	NON IMAGING APPLICATIONS	13
4.1	HIGH POWER LASERS	13
4.2	GLASS LASERS	15
4.3	COATING MATERIALS	16
4.4	OTHER APPLICATIONS	17
5.0	IMAGING APPLICATIONS	18
5.1	PARTIAL DISPERSION CHARACTERISTICS - n and v	19
5.2	SPECIFIC FORMS	26
5.2.1	FORM 1: RECOMMENDED BY M. HERZBERGER	29
5.2.2	FORM 2: RECOMMENDED BY J. HOOGLAND	30
5.2.3	FORM 3: RECOMMENDED BY K. BYSTRICKY	32
5.3	OTHER DESIGN CONSIDERATIONS - n ONLY	33
5.3.1	ABERRATION CORRECTION WITH HIGH INDEX MATERIALS	33
5.3.2	VARIABLE INDEX	38
6.0	CONCLUSION	44
	REFERENCES	46
	APPENDIX I	48
	APPENDIX II	53
	GLOSSARY	61

LIST OF FIGURES

Figure 1.	Ultra-Violet Transmission (thickness 5mm) Of Various Materials.
Figure 2.	Ultra-Violet Transmission Of Schott Optical Glasses (thickness 5mm).
Figure 3a.	Comparison Of Dispersion Curves For A Variety Of Schott Glasses.
Figure 3b.	Comparison Of Dispersion Curves For A Variety Of Schott Glasses.
Table 1.	Comparison Of Relative Partial Dispersions For Various Schott Glass Types.
Table 2	Index Values For BaF7 And A Desired Variation VAR5.
Table 3.	Index Values For BaK5 And A Desired Variation VAR11.
Figure 4.	Plot Of P^{**} Against P^* For Various Materials.
Figure 5.	Deviation From Normal Partial Dispersion Versus Dispersion.
Table 4.	Normalized Longitudinal Spherical Aberration Associated With Introduction Of A Flat Transparent Plate Into A Focussed Beam.
Figure I-1.	Deviation From Normal Partial Dispersion Versus Dispersion.
Figure I-2.	Relation Between Distance Ratios And ΔX Ratios In Figure I-1.
Table II-1.	Index Values For BaF7 And A Desired Variation VAR5.
Table II-2.	Index Values For BaK5 And A Desired Variation VAR11.
Figure II-1.	Index Variations Of VAR5 And VAR11 From Their Base Glasses.
Figure II-2.	Photographic Objective Considered In Computations.

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1.0 SUMMARY

The use of new glasses for optical components and systems requires a knowledge of the optical properties over the spectral range for which the optic is to be used. Specific applications may be identified as a function of index only, provided that the material possesses physical properties consistent with the proposed use. For example, the possibility of obtaining microscopes with increased numerical apertures (i.e. smaller relative apertures or f/no.'s) is strengthened by the availability of higher index materials. Furthermore, high index fibers for fiber optic systems means that the fiber bundles can be curved into tighter circles. Residual field curvature for photographic objectives and mapping lenses can also be reduced with high index glasses.

Other applications require assumptions about desirable index and dispersion properties that could yield improved performance for astronomical objectives, reconnaissance lenses, multi-spectral cameras, and other photographic systems. For example, photographic astrographic lenses used for precise determination of star positions require extremely small chromatic distortion of the star images. By obtaining glasses with a greater variety of index and reciprocal dispersion, optical designers will be able to achieve more highly corrected forms of these lenses.

There are other applications which require improvement of properties other than n and ν . In many window systems as well as in monochromators and spectrometers, it is desirable to obtain components with improved trans-

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mission characteristics, especially in the U-V and I-R regions. For example, there are currently no glasses which transmit light in the spectral region around 1000\AA , and highly dispersive lead glasses exhibit absorption bands in the near U.V.

As a result of these many requirements, it is therefore felt that increased effort to the fabrication of these new glasses be expended so that the relevant opto-mechanical properties may be measured directly. In this way, accurate data will be available to use as input for ray tracing and design optimization routines as refinements for explicit lens forms are sought to achieve improved performance.

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2.0 INTRODUCTION

The newly proposed method for manufacturing glass which is currently under investigation by North American Rockwell (NR/SD) derives its appeal essentially from the two following points: first, it may allow glasses to be made from materials not previously attainable in the glass state; secondly, these glasses will be of ultra-pure content, probably remaining as pure as the raw materials used to produce them. The first attribute suggests that materials exhibiting a new variety of optical, mechanical, and thermal properties may become available for use in optical imaging systems. The second suggests that materials of improved transmission performance may also be available for such systems. Purity control is also desirable in several systems which employ glass for reasons other than its imaging characteristics.

Applications based primarily upon the availability of glasses with new index and dispersion properties are best explained in terms of the techniques and limitations of optical design and will be explained in the latter part of this report.

In addition to a glass type's index and dispersion characteristics, factors such as its transmission, homogeneity, and scatter characteristics as well as its thermal stability (of index, size, and shape), environmental susceptibility, and manufacturing compatibility are all considered during the process of selecting the most desirable glass for a given application. There exist situations, especially if a glass is to be used as a modulator or laser rod, or as an optical component in J.V. or I.R. transmitting systems, where its desirability is more dependent on these factors than on

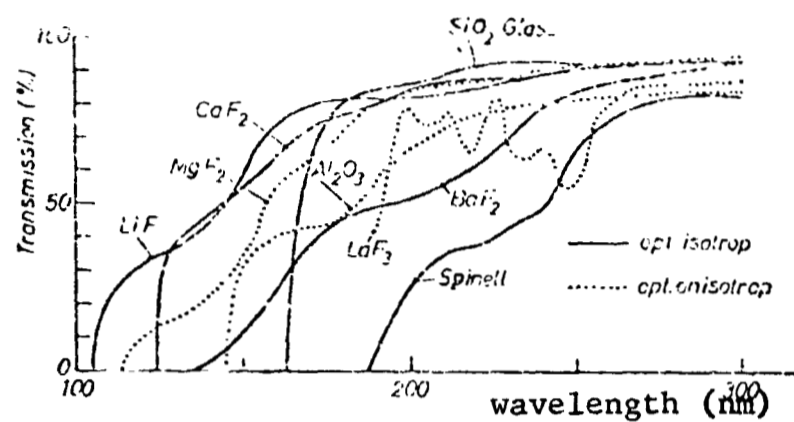
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index related ones. Since, in any case, the desirability of a glass type exhibiting unusual index behavior could only be enhanced by the additional improvement of these other characteristics, it seems appropriate to discuss these factors first. An overall summary of existing limitations will be supplemented by descriptions of the advantages and disadvantages of currently existing materials in order to provide the best idea of the type of improvements which would be most beneficial. The materials discussed will be classified according to their region of applicability such as in U.V., I.R., or visible transmitting systems or non-imaging devices.

3.0 MATERIALS

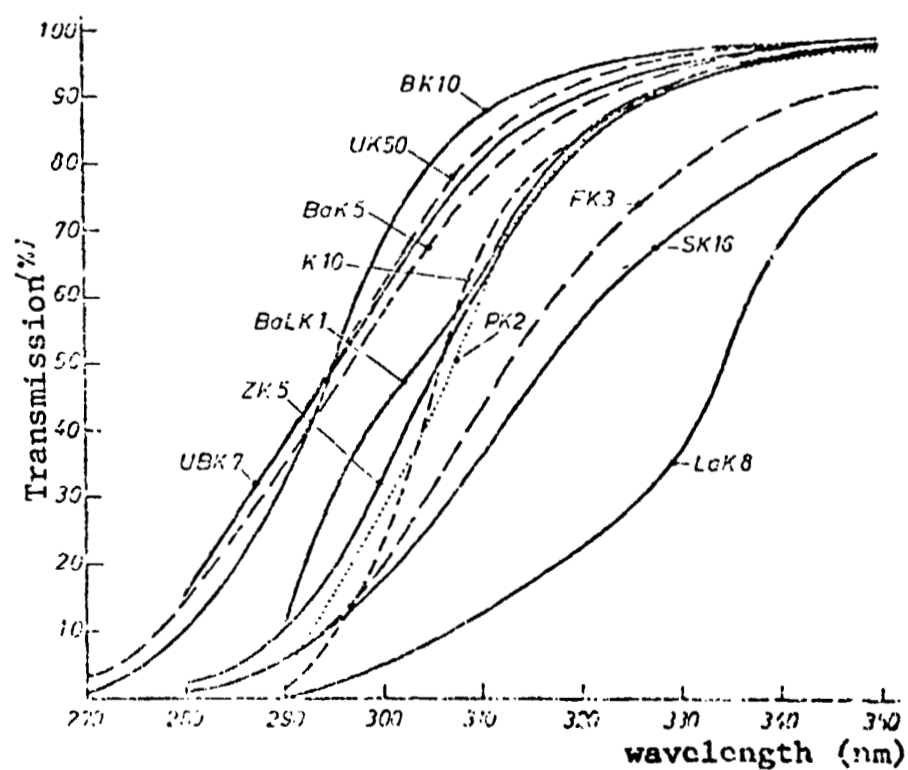
3.1 General Limitations

The limited transmission range achievable with existing optically useful materials remains an unsolved problem in the development of U.V. and I.R. transmitting systems.¹ The vacuum U.V. extends at least down to 584\AA (strong helium line) before one encounters an overlap with soft x-rays and hard U.V. rays. Absorption bands, primarily due to electron transitions, occur in all available materials well before this cut off. A plot of the ultraviolet transmission for a number of crystal materials is shown in Figure 1, and that for some of the available Schott glasses is shown in Figure 2. It is apparent that the crystalline fluorides and oxides transmit the farthest. Lithium fluoride, LiF, exhibits the longest U.V. transmission, but at 1215\AA (Lyman α) it is down to 50%. The available glasses transmit only in the near U.V. just before the atmospheric absorption band



UV TRANSMISSION OF VARIOUS MATERIALS
(Thickness 5mm)

FIGURE 1.



UV TRANSMISSION OF SCHOTT OPTICAL GLASSES
(Thickness 5mm)

FIGURE 2.

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and even the performance of these is impaired by the presence of trace impurities. The presence of impurities such as lead, iron, cerium, and titanium can affect the transmission differently depending on whether the melt was performed in a reducing or oxidizing atmosphere. Thus currently, space oriented V.U.V. and X.U.V. instruments require all reflecting components from at least 1215\AA down. This would suggest the existence of potential applications for new glasses of improved transmission in this region.

The selection of materials with transmission suitable for use in the Infrared region is similarly limited.¹ Glasses, of course, would be more desirable than crystals because of their isotropic nature and lack of directional properties associated with some crystal structures, but crystal materials to date exhibit more desirable transmission characteristics. Most of the oxide based glasses have long wavelength cutoffs in the 2 to 3 micron range imposed by vibration absorptional effects. In addition, absorption bands due to impurities of water and OH radicals are usually apparent. Attempts to develop oxide glasses of higher purity led to glasses of lower index. Thus use of these glasses requires components of greater thickness (and therefore, increased absorption and weight) and more severe curvatures (and consequently worse imaging performance), both undesirable side effects as explained later. Other non-oxide glasses have been developed which exhibit cutoffs in the 12 to 19 micron region, but they are characterized by other undesirable material properties as

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outlined in the examples below. The same is true of the ionic crystals and polycrystalline materials which exhibit superior I.R. transmission characteristics.

In addition to limitations on the transmission performance of available materials, limitations related to materials' thermal stability, environmental susceptibility and manufacturing compatibility impose the most severe remaining problems.

Whenever an optical system is subject to strong thermal shock (such as projection condensers) or required to maintain extreme stability in the presence of temperature variations (such as laboratory instruments or system windows), factors such as variations of expansion (α) and index (dn/dT) with temperature become of primary importance in the selection of component glasses. A common figure of merit used for comparing materials is the quantity $\Gamma = dn/dT + \alpha(n-1)$. In these terms, materials exhibiting low Γ values are most desirable but not currently available. Fused silica is the only glass with a low expansion coefficient, α , which is also of sufficient homogeneity to use in imaging systems, but its change of index with temperature is undesirably large. Obviously an increased variety of acceptable glass types would be appealing.

Focal plane surfaces, film tracks, and eye pieces subject to constant cleaning, as well as windows and bubble chambers, are some of the types of applications which require materials with a good resistance to either mechanical or chemical abrasion or radiation. For

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other applications soft or hygroscopic glass may be coated or used in a protective environment, but it is always desirable to be able to avoid the need for such measures.

Finally of general importance, is the ease of workability of the glass. It would be desirable to use present manufacturing techniques to figure any new glasses. Many crystalline materials presently used in monochromators and spectrometers, although exhibiting good transmission characteristics, are hard to figure because they respond differently to polishing in various directions. Other materials such as sapphire, will be difficult and time consuming to figure because of their extreme hardness. It should be confirmed that current techniques such as grinding and polishing procedures may be used with the new glasses without inducing crystallization.

3.2 Specific Properties

Some current materials used for U.V. Transmitting Systems include the following:¹

1. Lithium Fluoride - As mentioned before, this crystalline material transmits well from about 6μ to 1200\AA . However, the transmission toward the 1200\AA end is impaired because of the existence of impurities. It is currently used to make prisms, windows, and lenses for use in the vacuum U.V.
2. Calcium Fluoride - The existence of impurities in crystalline material of this type causes it to fluoresce in the U.V. (If

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pure, this material would be useful in U.V. microscopes which require a high N.A.,* thus even small quantities would be useful.) Its present uses are similar to those of LiF.

3. Magnesium Fluoride - This material is a relatively good U.V. transmitter. It would be desirable in glass form since problems exist due to its crystalline nature. However, the glass form is useful only if extreme purity can be preserved.
4. Fused Silica - This is one of the current materials potentially suitable for use in the ultraviolet region. It is available as crystal quartz or fused silica glass. Weak traces of impurities such as iron, lead, titanium, and cerium, however, reduce the U.V. transmission of this material. Moreover pure fused silica glass is isotropic. When it contains slight impurities, however, it becomes anisotropic. Since it is commonly used as a field lens in spectrometers where the incident light is generally polarized, its anisotropic nature rotates the polarization and consequently induces erroneous changes in output readings.

In summary, it is first apparent that if only existing materials could be processed by the proposed NR/SD method, they would be desirable because of their improved transmission characteristics. Secondly, existing crystals are generally hygroscopic and difficult to work, and even if not hampered by impurities, do not transmit well over the

* The notation N.A. will be used throughout the report to represent Numerical Aperture.

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entire U.V. range. Thus, the development of completely new glasses might be desirable either in order to obtain glasses with improved physical characteristics, or to obtain glasses with extended transmission ranges in the vacuum U.V. or, ideally, to achieve both. Further applications of materials with improved U.V. transmission and high index might also be found in fiber optics for these short wave regions. The relevant properties required of the materials for this application are discussed later.

Some materials available for use in the I.R. are described below:¹

Common Oxide-based Glasses ($\text{SiO}_2, \text{B}_2\text{O}_3, \text{P}_2\text{O}_5$)

Most of these glasses have good visible transmission but very limited usefulness in the I.R. Typical long wavelength cut offs are in the 2 to 3 micron range. Due to impurities of water and OH radicals, these glasses have absorption bands at 2.9 - 3.2 microns.

Infrasil and Suprasil (registered trademarks of Amersil, Inc.)

These are high purity fused silica glasses. This high purity e.g., less than five parts per million of water or OH allows a high transmission through the visible spectrum and out to 3.5 microns. If used in thin sections, i.e. 10mm thickness, absorption at 2.7 microns is considered negligible, whereas when used in thicker sections of 30-100 mm transmission is seriously affected. Because of their low refractive index (1.4 at 2.5 microns) larger thicknesses and severe curvatures are required

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to achieve a given correction.

Heavy Ion Oxide-based Glasses (Aluminate, gallate, telluride glasses)

It has been found that the addition of glass formers having large ions and weaker interatomic bands tends to extend the I.R. cut-off to longer wavelengths. The transmission range of these glasses, defined as the 50% level (i.e. equal transmission and absorption), is approximately .35 to 5.5 microns for thin (0.080 inch) sections.

Monoxide Glasses-Chalcogenide Glasses (Sulphide, selenide, telluride, arsenide glasses)

The transmission of these glasses typically extends from the visible (As_2S_3) or near I.R. (selenides) out to the 12 or 19 micron region. Some of these chalcogenide glasses unfortunately are soft, have low melting temperatures, and are subject to cold flow. They are characterized by very low absorption coefficients and thermal conductivities, high expansion coefficients and refractive indices.

Ionic Crystals CaF_2 , KBr, KCl

Most of these crystals have good transmission and mechanical strength but poor (low) refractive indices and (high) thermal expansion coefficients. Many are hygroscopic, and as such show poor durability and transmission characteristics with the passage of time in humid environments. As a class they have good trans-

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mission in the visible through mid-I.R. regions. They are, however, subject to cold flow, and have poor durability and isotropy.

Hot Pressed Polycrystalline Materials (from Eastman Kodak, and IRG materials from Schott)

These generally show poor homogeneity and high scatter due to the existence of residual internal pores and grain boundaries between crystals. This renders them inappropriate for critical I.R. applications. In addition, preferred crystallographic orientation is common and results in directional variations in selected optical properties.

Semiconductive-Materials (Silicon and Germanium)

These semiconductive materials are both crystalline solids and are available as single crystals and polycrystals. Polycrystalline forms of up to approximately 20 inches in diameter are made by crystal growth processes (the Czochralski and Bridgmann crystall growth methods). The high index of these materials results in improved performance of imaging designs. It might be convenient to have them in glass form to avoid some of the above mentioned problems of crystals and polycrystals.

In summary it can be seen that most previous attempts to produce materials for use at long wavelengths have resulted in materials which were inferior in other aspects such as index, scatter, homogeneity, or durability. Many of these are also crystalline forms whose anisotropic nature and directional properties are not desirable.

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The semiconductor materials silicon and germanium seem to be quite desirable because of their high refractive indices and good transmission properties. Further advantages might be gained if they could be obtained in the glass form.

The various types of glasses currently available for use in the visible region are well known. It should suffice at this point to note that there presently exist borate, and phosphate glasses as well as glasses containing fluorines and fluorides which exhibit desirable transmission in this region. These glasses are characterized also by desirable partial dispersion variations such as those described in later discussions. Borate and phosphate glasses, however, are too unstable to use and the fluorine based ones, although useable, are soft, fragile, and readily susceptible to weathering. These serve as prime examples supporting the statement that a glass type's desirability is dependent on more than simply its index characteristics.

Finally there remain a few miscellaneous applications for glass materials as described below which may benefit from the NR/SD process because of its potential for providing glasses of improved purity.

4.0 NON-IMAGING APPLICATIONS

4.1 High Power Lasers

Recent advances in high power lasers have identified physical characteristics of optical components which might not ordinarily be

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considered for the same spectral region using conventional sources. The problem is particularly acute for CO₂ applications; to quote, "There are no presently available materials which have acceptable physical properties for aircraft applications at 10.6 μ m at the power levels and window sizes of interest."³ Since this particular application is for monochromatic radiation, dispersion is not important, however, the author has identified that low indices of refraction are desirable. Furthermore, very low absorption at 10.6 μ m is mandatory. Since the materials which transmit in this region include metals and insulators, the absorption can take place as a result of different physical phenomena. Specifically, absorption can result from free carriers, i.e. electrons and holes, the lattice structure of crystals, imperfections and inelastic scattering. Since the absorption coefficient is proportional to the electrical conductivity and the strength of the E field squared, metals and high conductivity semiconductors are not suitable. However, insulators and low conductivity semiconductors are applicable since there are not enough free carriers in these materials.

Lattice absorption occurs when the transverse field causes the positive and negative ions in the crystal to move in directions opposite and perpendicular to the direction of propagation. What happens is that energy is transferred from the electromagnetic wave to the crystal thereby causing it to heat up. If the NR/SD technique for melting crystals to form glasses could be applied here, then

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effectively the lattice structure would be upset and perhaps the absorption phenomena could be circumvented. Absorption due to imperfections and impurities could also be reduced with the proposed methods. Discussion of this point and the effect of these impurities in other regions of the spectrum are discussed in subsequent sections.

4.2 Glass Lasers

The use of glasses and crystals for host materials in $1.06\mu\text{m}$ laser applications has been summarized recently by a number of authors.⁴ Some of the ions which have been made to lase in glass include Nd^{3+} , Yb^{3+} , Er^{3+} , and Mo^{3+} .⁵ Of the crystalline hosts, yttrium aluminum garnet (YAG) is the best commercially available material. Others include the rare earth oxides and a number of fluorides. The advantage to use of crystals over glasses is their higher thermal conductivity and narrower fluorescence linewidth. The major disadvantages are being inhomogeneity and anisotropy.

Glasses on the other hand can be doped more homogeneously but they have broader fluorescence lines and lower thermal conductivities. As a result, thermally induced birefringence and distortion occur when they are used at high powers and pulse rates. Although the ordered structure of crystals would be upset when transformed to a glass thereby lowering the conductivity, the possibility exists that a glass with higher conductivity than is currently available might be produced with the NR/SD techniques. Crystals currently possessing

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very high conductivities would therefore be likely candidates for glass laser host materials.

4.3 Coating Materials

Refractory Oxide materials are potentially some of the most useful coating materials available. They are almost without exception, capable of producing the hard, durable chemically resistant films that are required to meet stringent military environmental specifications.

The materials cover a wide range of refractive indices from the low of 1.46 for SiO_2 through the higher values of 2.15 for ZrO_2 and 2.6 for the rutile form of TiO_2 . The materials that are particularly valuable are the medium index materials Al_2O_3 , MgO , HfO_2 which are useful in the design of durable broad band AR coatings.

In practice many of the materials are difficult to evaporate. Extremely high temperatures produced by electron beam sources are required for their evaporation. At these high temperatures there is a strong tendency for the oxides to decompose into metals and sub-oxides, producing films with excessive absorption. The chance of decomposition in the materials is invariably stronger if the materials are not in the most pure form.

The behavior of the materials in electron beam sources in some cases can be erratic. MgAl_2O_4 in its natural, Spinel, form is subject to decrepitation and explosions due to inclusions and faults in the

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crystal particles. This leads to very highly scattering films and films which may contain embedded particles of substantial size. This is unfortunate as MgAl_2O_4 has some useful properties particularly in that it forms films with low internal stress and forms hard films without the need for high substrate temperature during deposition.

We have recently performed experiments with the evaporation of G.E. "Yttralox" material. This material is a mixture of Yttrium Oxide and Thorium Oxide (Approx. 9:1) in glassy form. Behavior in the electron beam gun was excellent and the films formed were essentially absorption free. The same materials as powdered chemicals are difficult to manage and are prone to decompose and give absorbing films.

Should other refractory oxide materials become available in glassy form, it would be interesting to explore their use as coating materials and compare them with existing forms. The results of these experiments could be of extreme value to manufacturers and designers of multilayer thin film devices.

4.4 Other Applications

Other more recent applications would be in the use of crystal modulators⁶ (e.g. Lithium Niobate). Intermetallic oxides have been developed for use with laser radiation as modulators or functional simulators. Their performance depends on their purity. In addition, semiconductor alloys⁶ (e.g. Gallium Arsenide) are currently being used as optical components for the I.R. such as laser windows and

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active elements. If their purity content could be controlled (not necessarily eliminated) say by controlling the purity of the raw materials only, one could achieve desired optical effects.

5.6 IMAGING APPLICATIONS

It seems possible that the NR/SD techniques may offer new methods for fabricating optics with more of the desirable properties outlined in the previous discussions. In any event, the initial data supplied for the candidate glasses indicates that the new glasses will at least be characterized by new n_D, ν_D combinations. Thus, the potential applications which may stem from the availability of glasses with new index and dispersion properties will be discussed in the remainder of the report.

A review of Kingslake's ⁷ description of basic optical design techniques suggests that the provision of new glasses which exhibit combinations of refractive index and dispersion appreciably different from those on the present $n_D - \nu_D$ diagram may be expected to have a desirable impact on current optical designs. However, the exact nature of all anticipated improvements and simplifications which might result from their use may be difficult to completely specify. He defines the designer's "degrees of freedom" as those elements in the structure of a lens which are available for change as a design is optimized. Included among the basic "degrees of freedom" are the radii of curvature of the surfaces, the thicknesses and air spaces, and the refractive indices and dispersive powers of the component glasses. In addition, there are some secondary "degrees of freedom" based on either

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clever use of the interface between two cemented surfaces or the use of symmetry. In particular, Kingslake describes the following uses of interfaces:

1. The curvature of a "buried surface" or a surface which separates two media of equal index but differing dispersions may be used to correct chromatic aberration without affecting other corrections.
2. An interface separating two media of equal dispersion and very nearly equal index may be used to obtain non-proportionate changes in ray deviation with incidence height.
3. An interface of weak curvature which separates two media of equal dispersion but widely varying index may be used to obtain a proportionate change in ray deviation with incidence light.

The desirability of an increased variety of index and dispersion combinations is thus readily apparent. The specific advantages of the increased "degree of freedom" may not become distinctly defined until, through experience, the designer has had an opportunity to see how the new characteristics will interface with currently available ones.

5.1 Partial Dispersion Characteristics - n and ν

One of the obvious areas which might capitalize upon the increased variety of index and dispersion combinations is the improvement or simplification of systems where achromatization and correction

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of secondary spectrum is a necessity.

High N.A. systems such as microscope objectives and low light level lenses, as well as long focal length lenses, such as reconnaissance systems and astronomical systems are particularly plagued by problems of secondary spectrum, since the magnitude of this aberration increases with focal length and N.A.

In the past the designers inability to control the effects of secondary spectrum in refractive designs made it necessary to use alternative reflective or catadioptric systems.⁸ Refractive systems are really more desirable, however, because of their smaller size and lighter weight. In general, they are also easier to package, can be readily folded and can incorporate an iris diaphragm and shutter if required. Thus with the recent introduction of improvements in the control of secondary spectrum refractive systems have become increasingly favored over reflective or catadioptric ones.

The basic problem associated with these systems stems again from the discussion of the designer's basic techniques.⁷ Since the designer is attempting to obtain a system of fixed focal length (and usually of fixed scale as well) any change in one "degree of freedom", such as is necessitated to go from color correction for two wavelengths to color correction at three or more wavelengths, must be offset by some other change in order to maintain the constant focal length desired. When glasses currently suitable for correction of secondary spectrum are introduced in the system, required compensations impair the achievable degree of monochromatic and color correction.

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As is well known, if the primary axial color of a system is corrected, the numerical value of the secondary spectrum may be determined from a relation of the form

$$S = (P_1 - P_2) / (V_1 - V_2) \quad \text{where } S = \text{Magnitude of Secondary Spectrum}$$

V_i = Dispersion value of D light for the i th glass type

and $P_i = \left| (n_D - n_F) / (n_F - n_C) \right|_i$

For a system corrected for C,F light this latter expression represents the D-F partial dispersion ratio of the i th glass type. Attempts to minimize this quantity result in the selection of glass types other than those customarily used in systems where secondary spectrum is not detrimental.⁹ Although one would like to choose glass pairs for which $\Delta P (=P_1 - P_2)$ is very small and $\Delta V (=V_1 - V_2)$ is very large, most existing glasses which exhibit similar P values also exhibit similar V values (maximum $\Delta V \approx 13$). In addition, they are generally of relatively low refractive index. When such glasses are used in place of conventional ones which are inappropriate for the correction of secondary spectrum, the design will necessarily contain components of increased individual powers (in order to maintain the specified focal length) which results in inferior monochromatic performance and increased chromatic variation of aberrations. Many of these side effects such as spherochromatism, zonal spherical aberration, and coma can be reduced at the expense of added complexity by selection of the proper lens form or adaptation or the use of aspherics.

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It would seem apparent that if secondary spectrum could be corrected by using glass pairs of the desired small ΔP , large ΔV characteristics, which were also of medium or high index, the design and use of complicated forms to counteract the side effects currently associated with the correction of secondary spectrum may not be necessary. For example, Schott Optical Glass Corporation recently introduced a new medium index crown glass called LgSK-2 which exhibits much greater departure from standard partial dispersion values. When considered in a design for an apochromat, element powers were reduced 30% from previous designs.⁶ Figures 3a, and 3b exhibit some n vs ν curves for various glass types including this new glass. Table 1 compares various partial dispersion ratios for some of the same glass types.

Another final example of the types of partial dispersion characteristics which might be desirable may be derived from Bystricky's work in 1968.^{10,11} At that time he theoretically investigated the potential improvement of a specific fast multi-element photographic objective (a design of Bystricky) that could be achieved through the use of new glasses which exhibit unusual partial dispersion characteristics. A summary of his approach is included as Appendix II. In his discussions he considered glasses which lie within the intermediate range of n_d and ν_d combinations rather than extreme glass types. By computing the resultant energy distribution in the image plane as he varied the partial dispersion characteristics of only the glasses used for two separate components, he was able to determine two

FIGURE 3a.

COMPARISON OF DISPERSION CURVES FOR A VARIETY OF SCHOTT GLASSES

GLASS TYPES REPRESENTED INCLUDE: FLUOR CROWN, SPECIAL SHORT FLINT, DENSE FLINT, TITANIUM FLINT, NEW GLASS TYPE LgSK2.

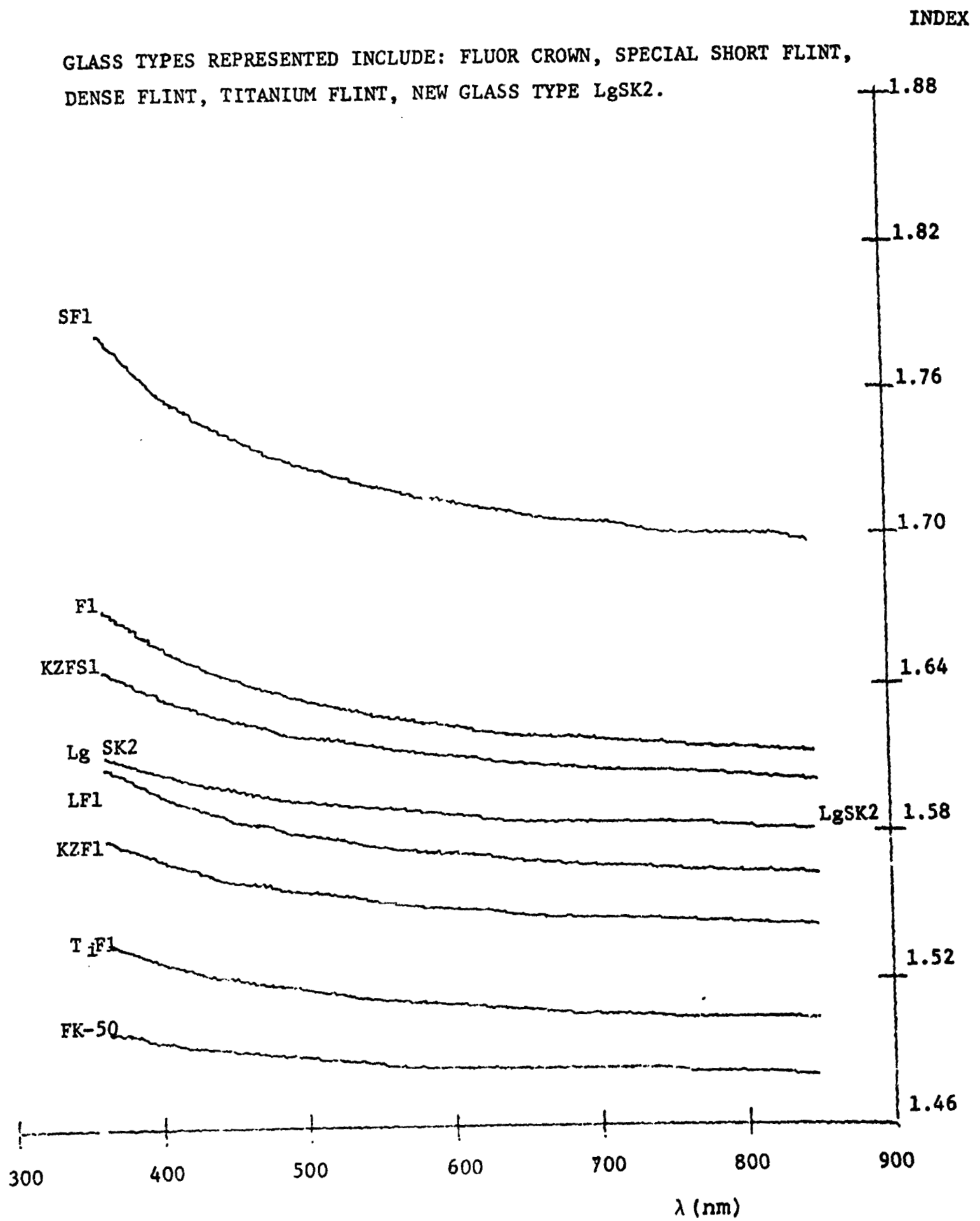


FIGURE 3b.

COMPARISON OF DISPERSIONS CURVES OF A VARIETY OF SCHOTT GLASSES

GLASS TYPES REPRESENTED INCLUDE: BARIUM FLINT, LANTHANUM FLINT, CROWN FLINT, EXTRA-LIGHT FLINT, PHOSPHATE CROWN, TITANIUM CROWN, NEW GLASS TYPE LgSK2.

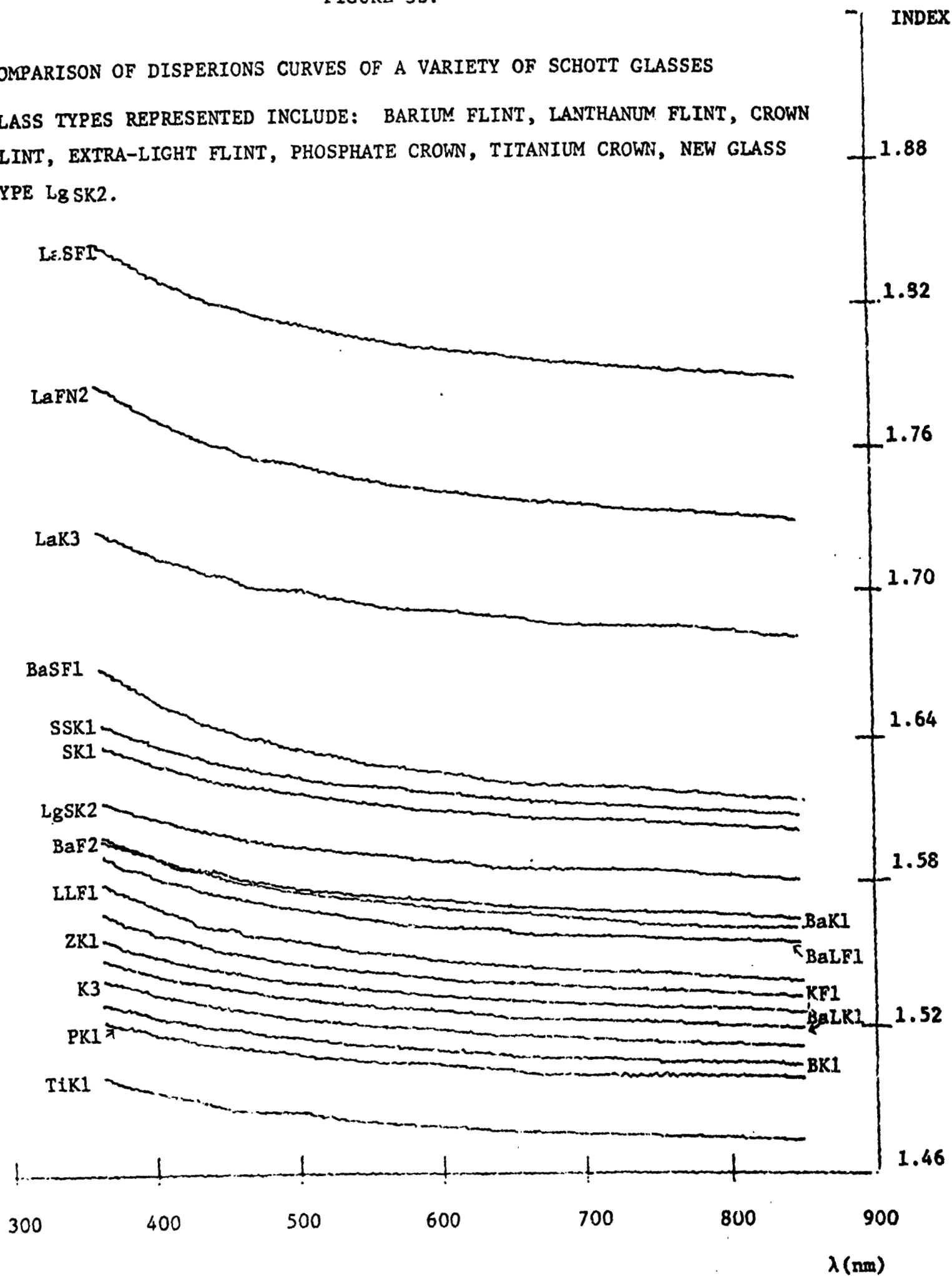


TABLE 1.

COMPARISON OF RELATIVE PARTIAL DISPERSIONS FOR VARIOUS SCHOTT GLASS TYPES

$$\Delta P_{\alpha,\beta} \triangleq (n_{\alpha} - n_{\beta}) / (n_F - n_C)$$

Glass Type	$\Delta P_{h,g}$	$\Delta P_{g,e}$	$\Delta P_{g,F}$	$\Delta P_{F,e}$	$\Delta P_{e,d}$	$\Delta P_{d,C}$
Lg SK2	.4622	1.015	.5534	.4614	.2383	.3003
FK-50	.444	1.044	.538	.456	.239	.305
PK1	.437	.984	.531	.452	.239	.309
BK1	.4441	.992	.5373	.4548	.2385	.3067
BaLK1	.4514	1.002	.5437	.4573	.2385	.3042
K3	.4526	1.002	.5443	.4576	.2383	.3041
ZK1	.4541	1.004	.5456	.4579	.2384	.3037
Bak1	.4552	1.007	.5470	.4587	.2383	.3030
SK1	.4564	1.007	.5479	.4589	.2384	.3027
KF1	.4710	1.019	.5576	.4615	.2380	.3005
BaLK1	.4712	1.021	.5585	.4622	.2379	.2999
SSK1	.4625	1.012	.5522	.4602	.2382	.2016
LaK3	.4597	1.010	.5506	.4599	.2383	.3018
LLF1	.4821	1.029	.5658	.4641	.2376	.2983
BaF2	.4740	1.054	.5605	.4629	.2379	.2992
LF1	.4897	1.037	.5714	.4659	.2374	.2967
F1	.5080	1.055	.5841	.4697	.2369	.2934
BaSF1	.5011	1.048	.5796	.4685	.2371	.2944
LaFN2	.4803	1.030	.5654	.4645	.2378	.2977
LaSK1	.4683	1.017	.5564	.4616	.2380	.3004
SF1	.5280	1.072	.5980	.4738	.2364	.2898
TiK1	.4529	1.002	.5441	.4570	.2384	.3046
TiF1	.4812	1.026	.5632	.4625	.2376	.2999
KZF1	.4692	1.017	.5564	.4612	.2379	.3009
KZFS1	.4729	1.020	.5581	.4611	.2377	.3012

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alternate glass types which could be used to slightly improve the chromatic image quality. The index values for these hypothetical glass types are specified for various wavelengths extending from 360nm to 760nm in Column 3 of Tables 2 and 3. He further noted that the substitution of several glasses each exhibiting less severe changes of the same trend could be used to obtain the same effect.

In practice the desired nature of the partial dispersion variations varies from design to design. Although it is possible to determine the desired variation for any given design by a process similar to the one Bystricky used in 1968, it is time consuming and tedious. Thus he suggested that although he is no longer associated with the particular design examined in his original report, one might first try to develop glasses with index variations similar to those derived in that report since they might be useful for other similar photographic systems and should provide an indication of the type of changes which are presently needed.

5.2 Specific Forms

Of the candidate glasses under consideration by NR/SD one would thus suggest the desirability of pairing a glass of the Nb_2O_5 - La_2O_3 - Ta_2O_5 region with one of the Al_2O_3 - La_2O_3 - SiO_2 region since they are at opposite ends of the dispersion curve. This however would be useful only if a pair of similar P values could be obtained. Since, unfortunately, no information is yet available about the various partial dispersion ratios which would characterize the candidate

TABLE 2.

INDEX VALUES FOR BaF7 AND A DESIRED VARIATION VAR 5

	Index BaF7	Index VAR 5	Δ Index BaF7 - VAR 5 $\times 10^5$
1	2	3	4
360	1,6439109	1,6482441	-433
380	1,6374185	1,6387929	-137
400	1,6321024	1,6322460	-14
420	1,6276770	1,6274335	24
440	1,6239420	1,6236928	25
460	1,6207526	1,6206403	11
480	1,6180015	1,6180494	-5
500	1,6156075	1,6157811	-17
520	1,6135076	1,6137490	-24
540	1,6116526	1,6118966	-24
560	1,6100033	1,6101853	-18
580	1,6085281	1,6083864	-6
600	1,6072014	1,6070863	11
620	1,6066020	1,6056639	34
640	1,6049126	1,6043096	60
660	1,6039184	1,6030137	90
680	1,6030072	1,6017683	124
700	1,6021687	1,6005665	160
720	1,6013041	1,5994029	199
740	1,6006757	1,5982724	240
760	1,6000071	1,5971703	284

TABLE 3

INDEX VALUES FOR BaK5 AND A DESIRED VARIATION VAR 11

	INDEX BaK5	VAR 11	INDEX BaK5 - VAR 11 $\times 10^5$
1	2	3	4
λ_{nm}			
360	1,5812819	1,5850847	-380
380	1,5770656	1,5795119	-245
400	1,5735388	1,5751255	-159
420	1,5705518	1,5715831	-103
440	1,5679952	1,5686622	-67
460	1,5657861	1,5662120	-43
480	1,5638613	1,5641271	-27
500	1,5621713	1,5623312	-16
520	1,5606773	1,5607679	-9
540	1,5593479	1,5593944	-5
560	1,5581581	1,5581774	-2
580	1,5570872	1,5570909	0
600	1,5561185	1,5561143	0
620	1,5552377	1,5552307	1
640	1,5544332	1,5544264	1
660	1,5536952	1,5536902	1
680	1,5530153	1,5530125	0
700	1,5523863	1,5523857	0
720	1,5518022	1,5518031	0
740	1,5512578	1,5512590	0
760	1,5507485	1,5507485	0

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glasses, it is impossible to predict whether or not the candidate glasses will have potential for this type of application. It might be recommended that determination of the Partial Dispersion ratios be completed as soon as possible since the range of applications for glasses which might simplify or minimize the problems currently associated with the correction of secondary spectrum seems quite extensive. If the information can be obtained, presenting it in one of the following forms may give additional information as to the potential usefulness of each of the glass types.

5.2.1 Form 1: Recommended by Max Herzberger¹²

Define

$$P^{**} = (n_F - n^{**}) / (n_F - n_C)$$

and

$$P^* = (n_F - n^*) / (n_F - n_C)$$

where $n^{**} = n$ at $\lambda = 1.01\mu$ for a given glass type

and $n^* = n$ at $\lambda = .365\mu$ for a given glass type;

and, Plot P^* vs P^{**} for each of the glasses.

The diagram of some current glass types is shown in Figure 4.

With these definitions, the achromatic properties of the glasses may be determined as follows:

1. Two glasses may be used to design an achromat-doublet corrected for two colors - if they are far enough apart on this plot so the components have reasonable powers.

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2. Any two glasses lying on a horizontal line may be used to design an apochromat corrected toward the violet region. Any two glasses lying on a vertical line can be used to design an apochromat corrected towards the infrared.
3. If three lens elements made of different glasses are used and the three characteristic points lie on any arbitrary straight line, one can design a superachromat (corrected for 4 colors) for systems of limited field angles.

This graph however, gives no clue as to the complexity or quality of the design which must be used in each case.

5.2.2 Form 2: Recommended by Jan Hoogland⁹

$$\text{Define } x = 1/\nu_e = (n_F' - n_C') / (n_e - 1),$$

$$y = (n_F' - n_e) / (n_e - 1),$$

$$y_{\text{normal}} = y_n = ay + b,$$

$$\text{and } Q = y - y_n,$$

where a and b are determined by any chosen boundary conditions.

Hoogland, for example, recommends that the line pass through points corresponding to glass types SK16 and SF2 (Schott). With these definitions a plot of the (x,Q) points for each glass type can be made. Such a diagram using some current glass types is shown in Figure 5. A detailed explanation of use of this diagram is contained in Appendix I. The powers of component lenses required to make an apochromat

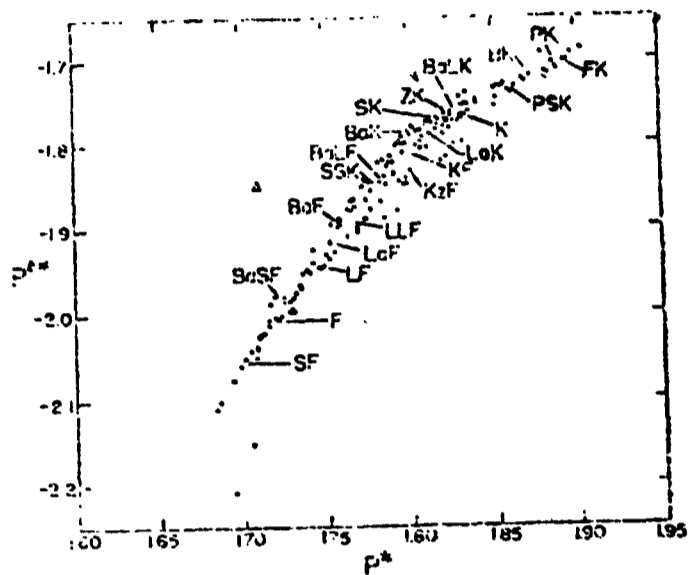


Fig. 4. PLOT OF P** AGAINST P* FOR VARIOUS MATERIALS

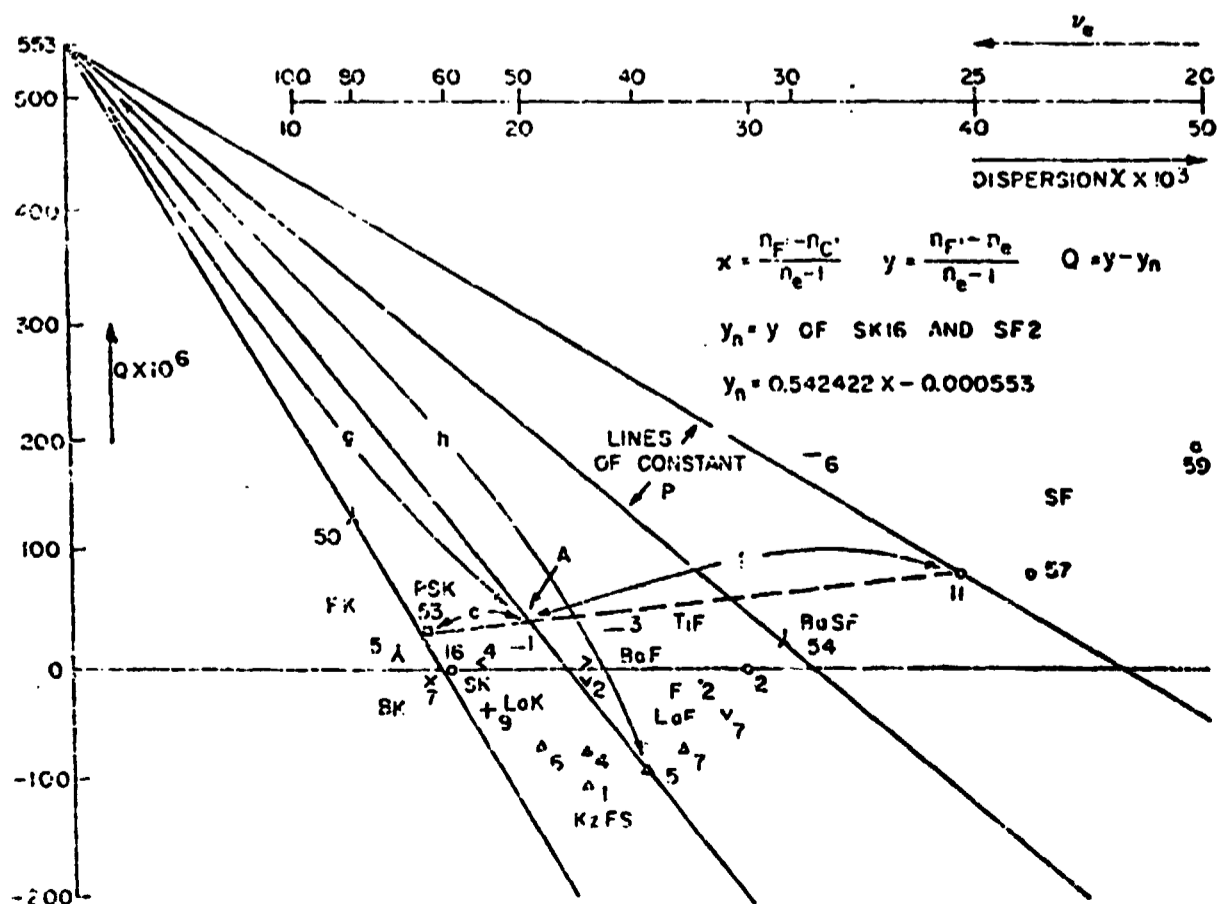


Figure 5. DEVIATION FROM NORMAL PARTIAL DISPERSION VERSUS DISPERSION

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corrected for C', e, and F' light may then be readily determined with the help of the graph. The magnitude of the powers gives an idea of the complexity and quality which can be expected in a lens.

5.2.3 Form 3: Recommended by Karl Bystricky¹⁰

Supply indices at the wavelengths listed below so the data may be interpreted in terms of a deviation function defined by δX which is related to the Abbe number, ν^x , and partial dispersion, P_x , by

$$\begin{aligned} P_x &= (n_x - n_1) / (n_2 - n_1) \\ &= B_x - D_x (\nu^x - \delta x / (n_2 - n_1)) \end{aligned}$$

Here B and D are constants for a wavelength $\lambda = \lambda_x$. Index information is required at the following wavelengths in order to determine B_x , D_x , and δ_x :

$$\lambda = 360 \text{ nm}$$

$$\lambda = 480 \text{ nm}$$

$$\lambda = 760 \text{ nm}$$

$$\lambda = 587.6 \text{ nm}$$

$$\lambda = 404.7 \text{ nm}$$

$$\lambda = 706.5 \text{ nm}$$

Using the deviation function, Bystricky can then apply his system for determining the expected indices at intermediate wavelengths and thus determine any desired partial dispersion ratio. Appendix II describes his approach in more detail.

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5.3 Other Design Considerations - n only

5.3.1 Aberration Correction with High Index Materials

Even in systems where correction of secondary spectrum is not required, an increased variety of index and dispersion combinations would enhance the designer's ability to correct other aberrations. Two specific areas which might (in the opinion of Kingslake)⁷ benefit include the design of anastigmatic photographic objectives and the design of aplanats.

For a system of separated thin lenses in air each of focal length, f , and index, n , the Petzval sum may be defined as follows:

$$\text{Petzval Sum} = \frac{1}{\rho} = \frac{1}{fn} \quad \text{when } \rho = \text{effective radius of curvature}$$

Kingslake states⁷ that this may be regarded as an indication of the expected residual field curvature which remains in the central field of a lens after the astigmatism has been removed. Conversely this sum may be taken as an indication of the amount of residual astigmatism which may be expected after the meridional field locus has been flattened. Thus to achieve a flat field free from astigmatism such as is desired in anastigmatic photographic objectives, this sum must be minimized. One technique helpful in achieving this is to pair high index low dispersive glass with low index high dispersive glass⁷. Increasing the variety of available glass types will thus increase the versatility of this technique.

In addition, Kingslake discusses the design of aplanats (lenses corrected for spherical aberration and ~~sine condition~~^{coma}) using conven-

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tional crown and flint glasses. There exist several current ways to correct these aplanats for one additional aberration, chromatic aberration, one of which uses the "buried surface" idea. He further suggests that a choice of different glasses (high index low dispersion and low index high dispersion) would be a more desirable approach. Extension of the variety of available index and dispersion combinations may thus find application here.

The existence of an increased variety of high index glasses irrespective of their dispersion properties may in itself be an advantage to lens design chiefly because it enables one to use individual components of less severe curvatures. It has been observed¹³ that image forming systems designed for use in the I.R. with components of high index semiconductor materials such as Germanium and Silicon are of appreciably superior quality than comparable glass systems primarily because of the weak curvatures which can be used. Unfortunately losses due to Fresnel reflections at boundaries are considerably higher as indicated by the following relation.

$$R = \frac{(N^1 - N)^2}{(N^1 + N)^2}$$

R = reflection coefficient
N¹ index of media after refraction boundary
N index of media before refraction boundary

Special antireflection coatings are thus necessitated to keep transmission levels high.

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Zoom lens designs might possibly benefit from the availability of high index glasses since the designer usually aims at maintaining constant values of the various aberrations of the zoom portion of the system while the focal length is varied and this process is aided by the use of relatively weak surfaces and narrow beam diameters.⁷

Other systems which might benefit from the ability to reduce the curvature of the component surfaces would be systems such as Spectrometers, Monochromators, and Polarizing Microscopes where the incident light is polarized.¹⁴ When plane polarized light is incident obliquely on a lens surface, the components in the plane of incidence and perpendicular to the plane of incidence are transmitted in differing degrees. The result is either a change in the plane of polarization (for linearly polarized light) or the state of the polarization (for circularly polarized light) across the aperture. This effect is currently treated by use of antireflection coatings, but could be decreased by reducing the necessary curvatures.

It has also been recently noticed¹⁵ that the aberrations introduced by the insertion of a flat transparent plate into a focused beam can be minimized by using glass of very high index. This is basically because incident rays for a plate of very high refractive index will pass through very close to normal. Thus all rays tend to be nearly parallel and neither tend to focus while in the plate, nor develop any aberrations. A table from the reference (Table 4) is included which lists the normalized longitudinal spherical aberration

TABLE 4.

Normalized Longitudinal Spherical Aberration Associated with Introduction of a Flat Transparent Plate into a Focused Beam

$$\delta f/l = n^{-1} - \cos\phi(1 - \sin^2\phi)^{-1/2}$$

n	ϕ	0.05 (2.9°)	0.10 (5.7°)	0.15 (8.6°)	0.20 (11.5°)	0.25 (14.5°)	0.30 (17.5°)	0.35 (20.5°)	0.40 (23.6°)	0.45 (26.7°)	0.50 (30.0°)	0.55 (33.4°)	0.60 (36.9°)	0.65 (40.5°)	0.70 (44.4°)	0.75 (48.5°)	0.80 (53.1°)	0.85 (58.2°)	0.90 (61.0°)
1.2	0.0013	0.0013	0.0013	0.0013	0.0013	0.0013	0.0013	0.0013	0.0013	0.0013	0.0013	0.0013	0.0013	0.0013	0.0013	0.0013	0.0013	0.0013	0.0013
1.4	0.0018	0.0018	0.0018	0.0018	0.0018	0.0018	0.0018	0.0018	0.0018	0.0018	0.0018	0.0018	0.0018	0.0018	0.0018	0.0018	0.0018	0.0018	0.0018
1.6	0.0025	0.0025	0.0025	0.0025	0.0025	0.0025	0.0025	0.0025	0.0025	0.0025	0.0025	0.0025	0.0025	0.0025	0.0025	0.0025	0.0025	0.0025	0.0025
1.8	0.0035	0.0035	0.0035	0.0035	0.0035	0.0035	0.0035	0.0035	0.0035	0.0035	0.0035	0.0035	0.0035	0.0035	0.0035	0.0035	0.0035	0.0035	0.0035
2.0	0.0050	0.0050	0.0050	0.0050	0.0050	0.0050	0.0050	0.0050	0.0050	0.0050	0.0050	0.0050	0.0050	0.0050	0.0050	0.0050	0.0050	0.0050	0.0050
2.2	0.0070	0.0070	0.0070	0.0070	0.0070	0.0070	0.0070	0.0070	0.0070	0.0070	0.0070	0.0070	0.0070	0.0070	0.0070	0.0070	0.0070	0.0070	0.0070
2.4	0.0095	0.0095	0.0095	0.0095	0.0095	0.0095	0.0095	0.0095	0.0095	0.0095	0.0095	0.0095	0.0095	0.0095	0.0095	0.0095	0.0095	0.0095	0.0095
2.6	0.0130	0.0130	0.0130	0.0130	0.0130	0.0130	0.0130	0.0130	0.0130	0.0130	0.0130	0.0130	0.0130	0.0130	0.0130	0.0130	0.0130	0.0130	0.0130
2.8	0.0170	0.0170	0.0170	0.0170	0.0170	0.0170	0.0170	0.0170	0.0170	0.0170	0.0170	0.0170	0.0170	0.0170	0.0170	0.0170	0.0170	0.0170	0.0170
3.0	0.0220	0.0220	0.0220	0.0220	0.0220	0.0220	0.0220	0.0220	0.0220	0.0220	0.0220	0.0220	0.0220	0.0220	0.0220	0.0220	0.0220	0.0220	0.0220
3.2	0.0280	0.0280	0.0280	0.0280	0.0280	0.0280	0.0280	0.0280	0.0280	0.0280	0.0280	0.0280	0.0280	0.0280	0.0280	0.0280	0.0280	0.0280	0.0280
3.4	0.0350	0.0350	0.0350	0.0350	0.0350	0.0350	0.0350	0.0350	0.0350	0.0350	0.0350	0.0350	0.0350	0.0350	0.0350	0.0350	0.0350	0.0350	0.0350
3.6	0.0430	0.0430	0.0430	0.0430	0.0430	0.0430	0.0430	0.0430	0.0430	0.0430	0.0430	0.0430	0.0430	0.0430	0.0430	0.0430	0.0430	0.0430	0.0430
3.8	0.0520	0.0520	0.0520	0.0520	0.0520	0.0520	0.0520	0.0520	0.0520	0.0520	0.0520	0.0520	0.0520	0.0520	0.0520	0.0520	0.0520	0.0520	0.0520
4.0	0.0620	0.0620	0.0620	0.0620	0.0620	0.0620	0.0620	0.0620	0.0620	0.0620	0.0620	0.0620	0.0620	0.0620	0.0620	0.0620	0.0620	0.0620	0.0620
4.2	0.0730	0.0730	0.0730	0.0730	0.0730	0.0730	0.0730	0.0730	0.0730	0.0730	0.0730	0.0730	0.0730	0.0730	0.0730	0.0730	0.0730	0.0730	0.0730

* See text

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introduced by the insertion of a flat transparent plate into a focused beam for various half angles ϕ . The asterisks represent the worst choice refractive index value for each case. The stepped solid line indicates index values for which a flat plate will produce less spherical aberration than a flat plate with refractive index of 1.2. Many of the candidate glasses indices are above 2.0. It can be seen from the Table that plates of such index will yield improved performance at half angles greater than 53.1° . Thus many high N.A. systems which require windows might benefit from the availability of this high index glass. They might also benefit dry microscope objective systems which require the use of a cover glass as discussed later.

The benefits of the use of weaker surfaces are not limited to these examples however. One would expect them especially to influence the design of lens of high speed and large size which currently necessitate components of high curvature. Since most candidate glasses are of high index, they might find such applications if they are stable and can be produced in large sizes.

Another isolated application which could benefit from glasses of an increased variety of index might be the universal stage which is used with polarizing microscopes to allow rotation of the specimen about several axis through its center.¹⁴ This is important for determining the optic axes and principal refractive indices of the specimen.

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The specimen when observed on this stage, is immersed in a layer of index matching fluid and located at the center of a pair of glass hemispheres also selected to approximate the index of the specimen. The basic idea is to keep the refractive effects of the specimen's surrounding media independent of rotation so that only specimen effects are observed. It would seem that an increased variety of reference hemispheres would increase the type of samples which could be accurately observed. The application, however, hinges on the development of matching index fluids as well since the present supply of high index fluids is limited and most exhibit color.

5.3.2 Variable Index

If in addition to creating glass of different indices it was found that the proposed NR/SD process could produce glass of controlled index stratification, design techniques might also benefit.

It has been determined that the distribution of the index of refraction of the crystalline lens of a rabbit eye may be described by a relation of the following form:

$$n = n_0 - \left[\frac{Z^2}{A^2} + \frac{(X^2 + Y^2)}{B^2} \right] \quad \text{where}$$

X lateral axis coordinate
Y vertical axis coordinate
Z optical axis coordinate
n₀ refractive index at the center of the lens

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When rays were traced through theoretical models exhibiting the same distribution, the lens seemed to exhibit decreased spherical aberration and increased refractive power relative to a uniform, n_0 , index lens of the same shape. In order to minimize spherical aberrations, there is an optimum relationship between n_0 and n of the crystalline lens.¹⁶ Thus it would seem that any system which benefits from reduced curvatures could similarly benefit from components of controlled index.

In addition, the use of graded index cylindrical glass rods as low resolution imaging relays has recently been introduced.¹⁷ Two distributions, the parabolic and the hyperbolic secant, have been suggested as sample distributions. They are described as follows:

1. parabolic

$$n(r) = n_A (1 - 1/2 \alpha^2 r^2)$$

2. hyperbolic secant

$$n(r) = n_A \operatorname{sech}(\alpha r)$$

where n = refractive index

r = distance to optical axis

n_a = index on the optical axis

$$\alpha = 2\pi/L$$

L = wavelength along the optic axis of the small amplitude oscillations or the ray path about the optic axis

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Some graded index rods of the parabolic distribution have been made by ion-exchange techniques.¹⁸ The introduction of the use of such rods led to an investigation of their imaging quality. The image aberrations noted for these relays are a function of the rod radius, object radius, and aperture angle. Thus one would expect the ideal desired distribution to vary from case to case. No ideal distribution has been determined yet which will provide good imaging of both meridional and skew rays, but analysis of the problem is continuing. The production of these rods will require precise control of the refractive index profile rather than control of absorption and scatter properties as is necessary for wave guides. However, if the imaging quality can be rendered comparable to that of a lens relay via computation of the proper distribution, the rod relay will exhibit advantages over the lens relay similar to those outlined in the ensuing discussion of fiber optic bundles.

In addition to the usefulness of high index glass toward the design of better quality systems there are a few conceivable cases including oil immersion microscopes and fiber optic bundles, where it may be used to obtain systems of higher numerical aperture.

In microscope systems the numerical aperture is a measure of the resolution as well as the light gathering ability of the objective.⁷ If S represents the smallest resolvable separation and N.A. represents the numerical aperture then

$$S = \lambda / 2 \text{ N.A.}$$

C3

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Thus it would appear that an increase in N.A. would be a desirable objective due to the associated increase in resolution. The cover glass which protects and holds the specimen is an inherent part of the microscope system. The development of the oil immersion microscope grew from the fact that by covering this glass slide with index matching fluid one could increase the effective useful cone of light emerging from the object, by eliminating refraction at the air glass interface above the glass cover. Since the N.A. may be defined as the product of the index, n , of the media in which the object lies, times the sine of the half angle, U_0 , which defines the limiting useful cone of light entering the objective,

$$\text{N.A.} = n \sin U_0$$

the numerical aperture of the oil immersion objective is thus higher than its counterpart dry objective. Currently covers and fluids of index 1.5 are used and the practical limit of achievable U_0 is about 71° . Such a combination exhibits a numerical aperture of 1.40. It would seem to follow that if both cover glasses and immersion fluids could be obtained with higher index values, the achievable N.A. and thus resolution could be increased still more. As was previously mentioned, however, useful high index fluids are not currently available.

The numerical aperture of a straight fiber optic bundle of core material of index, n_1 , and cladding material of index, n_2 , is

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defined by the following relation:

$$\text{N.A.} = \sqrt{n_1^2 - n_2^2}$$

provided that the diameter is much greater than a wavelength. Thus

the development of high index glasses for use as core material or

low index glasses for use as cladding material might enable the

formation of fiber optic bundles of increased numerical aperture.

It has also been determined that a greater variation in index between

the core and sheath materials increases the degree of bending or

tapering of a fiber which may be tolerated without detrimental transmission losses.

Although the field of Fiber Optics has developed greatly in recent years, its full potential may not yet be fully achieved. When used as a straight rod for transmission of light, the fiber optic bundle may be superior to an alternative lens system for the following reasons:¹⁹

1. The system has the capability of achieving a 90° acceptance angle.
2. The cladding material necessary to prevent "frustrated total internal reflection" also serves as a protective shield for the bundle. Thus bundles may be clamped, potted in resin, or lubricated without detrimental effects, and mounting considerations, thus, are considerably easier.

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3. Since only the ends of the bundle need positioning, rather than several component elements, the alignment of a bundle is easier than that of a lens relay.
4. Transmission losses from a straight line light guide result from the packing function, Fresnel losses at the end faces, and absorption within the glass. In general, if compared to a four or more element lens relay (uncoated) which suffers Fresnel losses at each surface, the fiber optic bundle will yield better transmission although the spectral distribution of the incident light may not be preserved.
5. Since the component fibers of a bundle may be arranged in any desired configuration, the bundle ends may be of differing shape but equal cross sections; thus they may easily be used to either essentially change the shape of an illuminating aperture, or convert a single illuminating source into several effective ones.

Applications, which capitalize on these five properties, already exist for straight line fibers and it would seem that the range of applications would be extended if only transmission performance could be maintained for curved or tapered fibers.

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For example, there currently exists a need for high N.A. fiber systems capable of withstanding extreme tapers or bendings called "twisters" to be used in conjunction with image intensifier systems to obtain an erect image. It has been empirically determined that a new glass of index 2.2 or higher with a transmission loss in the visible of less than 2 db/meter could be used in conjunction with existing cladding glasses to obtain a bundle capable of maintaining desired transmission characteristics while twisted 180° over about a 2" length.

Many of the candidate glasses exhibit index values over 2.2. However, their applicability toward use as fiber optic core material is dependent on many other factors as well. The material, for example, must show extremely low scatter and low absorption over the desired spectral range. Often, when used with C.R.T. devices, the glass must be compatible with that of the envelope of the C.R.T. in order to be useful. More importantly, however, it must be capable of withstanding the multiple reheating cycles involved in the present manufacture of fiber bundles without losing its glass properties. During these reheating cycles the core material is in contact with the cladding material. Because of these drawbacks it is premature to determine whether any of the candidate glasses would be useful in fiber optic applications or not.

6.0 CONCLUSION

As identified previously, many applications exist where knowledge of n

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at a single wavelength is all that suffices. For applications where optical design effort is required, it is mandatory that n be determined at many wavelengths in the region of interest to a precision comparable to current measurements of $\pm 5 \times 10^{-6}$. From a practical point of view the physical as well as the optical properties should be known so that materials can find broader applications, particularly in hostile environments.

A logical development from the work already achieved would be the production of small samples in the 12-25mm diameter size range under '0' g conditions. It is conceivable that this could be accomplished with an Aerobee payload. Samples of the size indicated could then be fabricated into plane parallel test specimens for the measurement of homogeneity, expansion coefficient, etc. In addition, prisms could be fabricated so that precise index measurements could be made. These experiments would establish two necessary conditions for subsequent work. First, they would demonstrate the feasibility of containerless melting for the production of glass much larger than with the current laser melting experiments. Second, the optical data could be used by the designers for computing specific improvements in standard lens forms such as in an astronomical objective or transfer lenses. Furthermore, the physical properties would allow assessment of the applicability of the material for use under different environmental conditions.

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APPENDIX I

This discussion describes the specific use of the chart proposed by Hoogland. The chart, Figure I-1, characterizes the various glass types by their (X,Q) point where

$$X \triangleq (n_{F1} - n_{C1}) / (n_e - 1) , \quad y \triangleq (n_{F1} - n_e) / (n_e - 1)$$

$$Q \triangleq y - y_n , \quad \text{and} \quad y_n \triangleq 0.542422X - 0.000553$$

These indices are those of a particular glass type at the indicated wavelengths.

If two thin lenses are used in contact to form a third composite lens, the composite hypothetical lens may be thought of as being characterized by an (X,Q) point also where the indices in question are the effective indices of the composite lens. The following derivation explains the relation between the distances between these three points as measured from the chart and the ratio of the powers of the two component lenses. The following notation is adopted:

ϕ_{ij} represents the power of a lens of the i th glass type at the j th wavelength.

n_{ij} represents the index of a lens of the i th glass type at the j th wavelength.

R_{ij} represents the quantity $(c_1 - c_2)$ of the lens formed from the i th glass type. c_1, c_2 , represent the curvatures of the two lens surfaces.

As an example, ϕ_{53e} represents the power of a lens of type 53 at the e line and ϕ_{ARE} represents the power of an artificial glass at the same line. The artificial glass could be selected from one of potential NR/SD candidates.

Thus for a triplet, the elements would have powers given by:

$$\begin{aligned}\phi_{53e} &= (n_{53e} - 1) R_{53} & \phi_{11e} &= (n_{11e} - 1) R_{11} \\ \phi_{53F'} &= (n_{53F'} - 1) R_{53} & \phi_{11F'} &= (n_{11F'} - 1) R_{11} \\ \phi_{53C'} &= (n_{53C'} - 1) R_{53} & \phi_{11C'} &= (n_{11C'} - 1) R_{11}\end{aligned}$$

$$\phi_{ARE} = (n_{ARE} - 1) R_{AR} = \phi_{53e} + \phi_{11e}$$

$$\phi_{ARF'} = (n_{ARF'} - 1) R_{AR} = \phi_{53F'} + \phi_{11F'}$$

$$\phi_{ARC'} = (n_{ARC'} - 1) R_{AR} = \phi_{53C'} + \phi_{11C'}$$

One can relate the powers of the component elements to their 'x' values as follows;

$$R_{AR} = (\phi_{53e} + \phi_{11e}) / (n_{ARE} - 1)$$

$$\therefore (n_{ARF'} - 1) \left[\frac{\phi_{53e} + \phi_{11e}}{n_{ARE} - 1} \right] = (n_{53F'} - 1) R_{53} + (n_{11F'} - 1) R_{11}$$

$$(n_{ARC'} - 1) \left[\frac{\phi_{53e} + \phi_{11e}}{n_{ARE} - 1} \right] = (n_{53C'} - 1) R_{53} + (n_{11C'} - 1) R_{11}$$

$$\left[\frac{n_{ARF'} - n_{ARC'}}{n_{ARE} - 1} \right] [\phi_{53e} + \phi_{11e}] = (n_{53F'} - n_{53C'}) R_{53} + (n_{11F'} - n_{11C'}) R_{11}$$

$$\left[\frac{n_{ARF'} - n_{ARC'}}{n_{ARE} - 1} \right] [\phi_{53e} + \phi_{11e}] = \frac{(n_{53F'} - n_{53C'}) \phi_{53e}}{(n_{53e} - 1)} + \frac{(n_{11F'} - n_{11C'}) \phi_{11e}}{(n_{11e} - 1)}$$

$$x_{AR} [\phi_{53e} + \phi_{11e}] = x_{53} \phi_{53e} + x_{11} \phi_{11e}$$

$$\therefore \phi_{53e} = \phi_{11e} [x_{11} - x_{AR}] / [x_{AR} - x_{53}]$$

Finally, it is apparent from Figure I-2 that

$$\cos \theta = (x_{AR} - x_{53}) / c = (x_{11} - x_{AR}) / f$$

$$f / c = (x_{11} - x_{AR}) / (x_{AR} - x_{53})$$

thus,

$$\phi_{53e} = \frac{f}{c} \phi_{11e}$$

Since the distances may be easily measured, this ratio is easier to use than that of the different X values.

In further explanation, if a combination is to be an apochromat corrected for e, F, c¹ light, its focal lengths must be equal at these wavelengths. If its power is represented by ϕ_{Tj} then

$$\phi_{Te} = (n_{Te} - 1) R_T$$

$$\phi_{TFI} = (n_{TFI} - 1) R_T$$

$$\phi_{TC'} = (n_{TC'} - 1) R_T$$

Thus for $\phi_{Te} = \phi_{TFI} = \phi_{TC'}$, $n_{Te} = n_{TFI} = n_{TC'}$

where these indices represent the effective index of the combination.

Thus, the hypothetical (X,Q) point for the apochromat must be (0, y_n) since

$$X_T = (n_{TFI} - n_{TC'}) / (n_{Te} - 1) = 0.$$

$$Q = (n_{TFI} - n_{Te}) / (n_{Te} - 1) - y_n = -y_n = -(ax + b) = -b$$

The following excerpt from Reference 3 is enclosed to demonstrate the calculation of the individual powers for one apochromat design:

"The powers required for an apochromat consisting of, for example, the glasses PSK 53, SF 11, and KzFS 5 are determined as follows:

The distances c, f, g, and h are measured (Fig.I-1). Then the ratios j and k are computed:

$$j = \frac{f}{c} = 4.36$$

$$k = \frac{h}{g} = -1.26$$

First, an artificial glass consisting of PSK 53 and SF 11 is formed at point A, the respective powers being ϕ_{art} , ϕ_{53} , and ϕ_{11} :

$$\phi_{ART} = \phi_{53} + \phi_{11}$$

$$\phi_{53} = j \phi_{11}$$

Then the artificial glass is combined with KzFS 5 to form an achromatic combination at point (0,553) and the total power is taken as unity:

$$\phi_{\text{art}} = k \phi_5 \quad \phi_{53} + \phi_{11} + \phi_5 = 1.$$

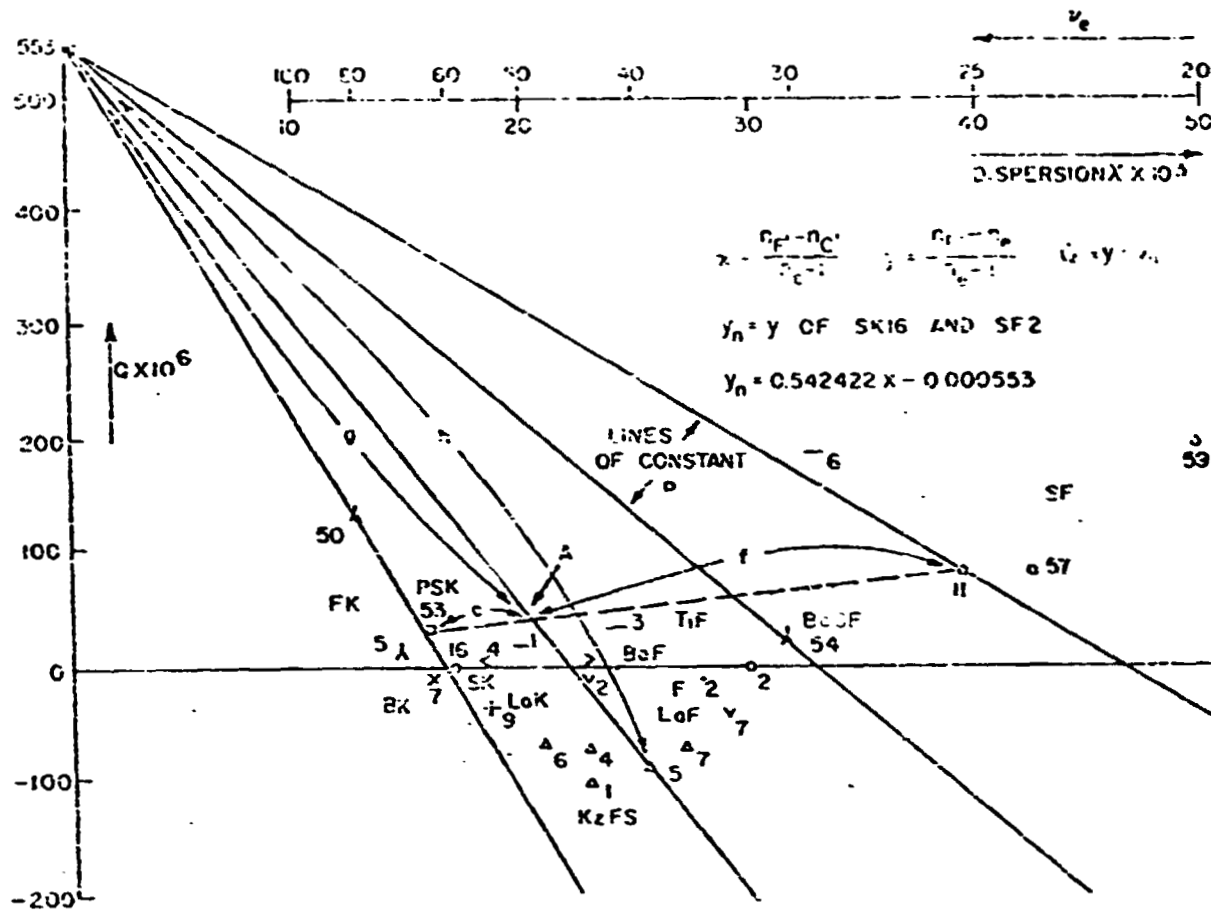
The combination is apochromatic because the components have the same P value.

For a short formulation of the end result, one defines $r = \frac{1}{j + k + jk + 1} = -0.72$

It follows that

$$\begin{aligned} \phi_{53} &= jkr = 3.95, \quad \phi_{11} = kr = 0.91; \\ \phi_5 &= (j+1)r = -3.86. \end{aligned}$$

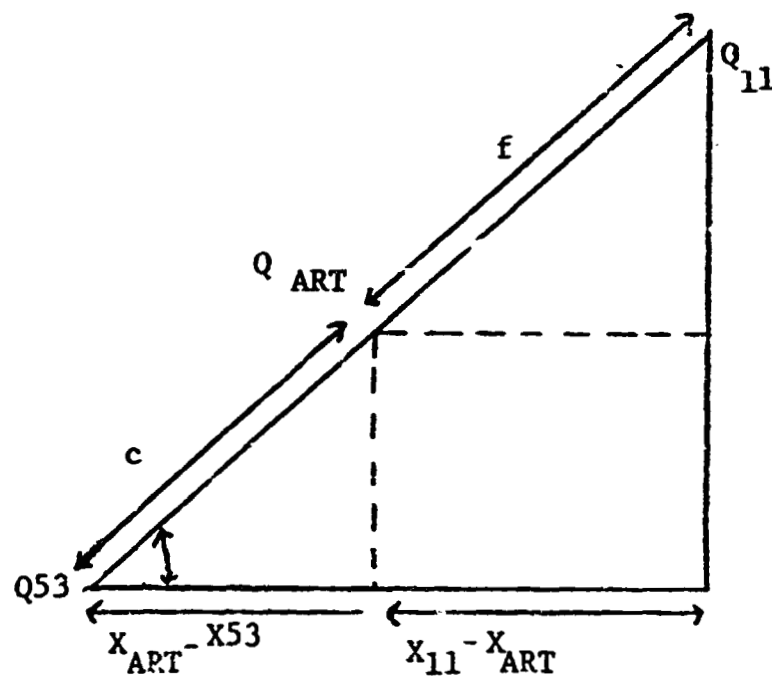
FIGURE 1-1



Deviation from Normal Partial Dispersion versus Dispersion

FIGURE 1-2

RELATION BETWEEN DISTANCE RATIOS AND ΔX RATIOS OF FIGURE 1-1



APPENDIX II

Bystricky has shown how a new system can be developed which allows specification of the refractive index of any glass type at any given wavelength if given prior knowledge of four (or) five proper constants. His approach essentially involves a refinement of Geffcken's dispersion formula.²⁰

$$n_x - 1 = (1 - D_x)(n_1 - 1) + B_x(n_2 - n_1) + D_x \delta_x$$

where n_x represents the refractive index of the glass at $\lambda = \lambda_x$

n_1 represents the refractive index of the glass at $\lambda = \lambda_1$

n_2 represents the refractive index of the glass at $\lambda = \lambda_2$

D_x, B_x represent universal constants which are dependent only on $\lambda_1, \lambda_2, \lambda_x$

δ_x is defined as the deviation function which describes the non linear variation of P_x for any glass type.

After dividing through by $n_2 - n_1$, the partial dispersion value P_x becomes:

$$P_x = (n_x - n_1) / (n_2 - n_1) = B_x - D_x (v^x - \delta_x / (n_2 - n_1))$$

$$\text{where } v^x = (n_1 - 1) / (n_2 - n_1)$$

Since for certain "normal glasses" the variation of P_x with v^x is linear and the deviation function is zero, estimates of B_x and D_x may be made from the following

$$\text{relation } D_x = \frac{P_x(\text{Ref. 1}) - P_x(\text{Ref. 2})}{v^x(\text{Ref. 1}) - v^x(\text{Ref. 2})} \quad B_x = \frac{P_x(\text{Ref. 2}) - P_x v^x(\text{Ref. 2})}{v^x(\text{Ref. 1}) - v^x(\text{Ref. 2})}$$

where, Ref. 1 represents the selected normal reference glass type #1, and Ref. 2 represents the selected normal reference glass type #2.

These calculations will be valid if the index values n_x , n_1 , and n_2 of the reference glass types can be accurately determined. Bystricky recommends the use of Schott Glass Types F2 and K7, the selection of the basic wavelength pair $\lambda_1 = 587.6\text{nm}$ and $\lambda_2 = 404.7\text{nm}$ or $\lambda_1 = 587.6\text{nm}$ and $\lambda_2 = 106.5\text{nm}$, and the use of Schott's dispersion for the most accurate determination of these constants.

(Schott's Dispersion Formula is as follows:

where the A_i are stated constants which are different for every glass).

$$n_{\lambda}^2 = A_0 + A_1 \lambda^2 + A_2 \lambda^{-2} + A_3 \lambda^{-4} + A_4 \lambda^{-6} + A_5 \lambda^{-8}$$

Secondly, he hypothesizes that there exists a bounded wavelength region over which

the variation of the deviation function appears linear for all glass types when

plotted against some properly distorted wavelength scale. The slope describing

the variation for any given glass type may be determined from known values of

the deviation function for that glass type (and thus knowledge of the refractive

indices of the glass) at the boundary wavelengths as long as the nature of the dis-

torted scale is known. He determined that for 200 of the 238 Schott glasses in

existence at that time, one distorted scale, derived from the distorted scales

which best describe glass types SF7, SF18, SF11, and SF58, was sufficient to

describe their deviation functions over the wavelength region extending from

360nm to 760nm, to within an accuracy of 1×10^{-5} . In Order to describe the de-

viation functions for the other 38 glass types to the desired accuracy, it is

necessary to subdivide the region into two smaller regions extending from 360nm

to 480nm and 480nm to 760nm and determine a representative distorted scale for each

region. To use the scale to determine intermediate values of the deviation function

for a given glass type values at the boundary wavelengths of each region must be

given.

Thus knowledge of the refractive indices of a glass type at two (or three) wavelengths plus knowledge of the distorted scale, are required to determine the deviation function of a glass at any other wavelength. In addition, the refractive indices at the basic wavelengths used to calculate B_x and D_x must be in order to calculate the remaining terms of the equation. He thus concludes that knowledge of the proper five index values for a given glass type as well as knowledge of the distorted scale is sufficient information to allow the determination of intermediate index values.

Since all "normal" glasses can then be characterized by their deviation function δ , one can hypothesize the behavior of a new glass by defining a new δ . Table 1 lists the index values as a function of wavelength for an existing glass type, BaF7 (Column 1), the index values for a glass type designated VAR5 based on BaF7 but derived assuming a different deviation function, (Column 2) and the difference in the 5th decimal place between the two values (Column 3). Table 2 lists the same data for existing glass type BaK5 and hypothetical glass type VAR11. Figure II-1 depicts the data of Column 3 graphically.

Finally the intensity distribution observed in several image planes for the standard fast photographic projection objective #103 (Figure II-2) which has the fourth element made of BaF7 glass and the second of BaK5 glass is compared with that observed for the variation of this design which substitutes VAR5 and VAR11 for those glasses.

One is able to distinguish improvements in the chromatic image quality of the varied system over that of the standard system. It should also be recognized that the same type of effect can be accomplished by small variations of the deviation functions of several lenses as by greater changes in only a few lenses.

On the other hand, the use of a few lenses exhibiting great changes may enable the elimination of one element from the design. It can thus be concluded that glasses showing partial dispersion characteristics similar to these hypothetical variations may be useful to the optical designer.

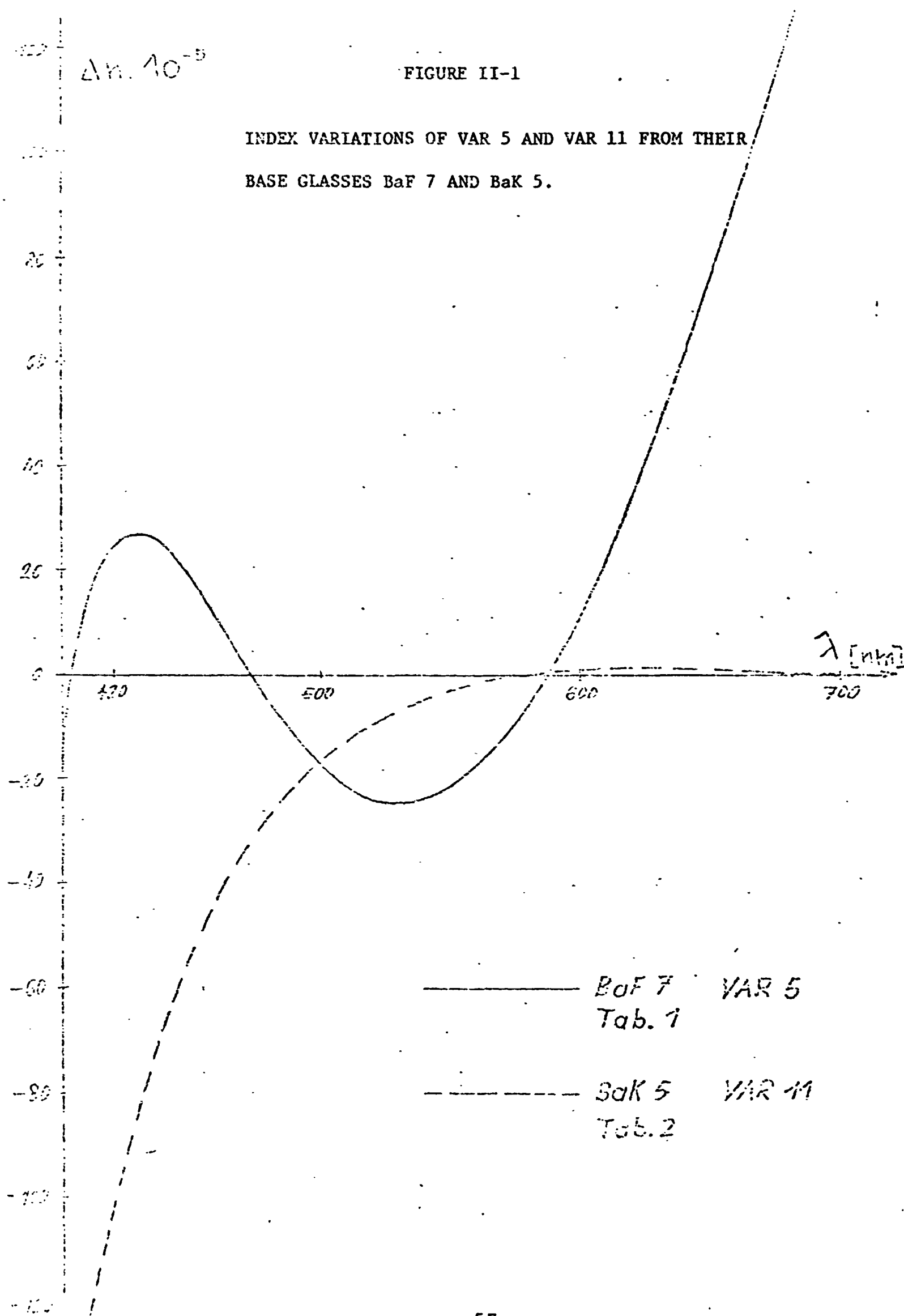


FIGURE I-2

PHOTOGRAPHIC OBJECTIVE CONSIDERED IN COMPUTATIONS

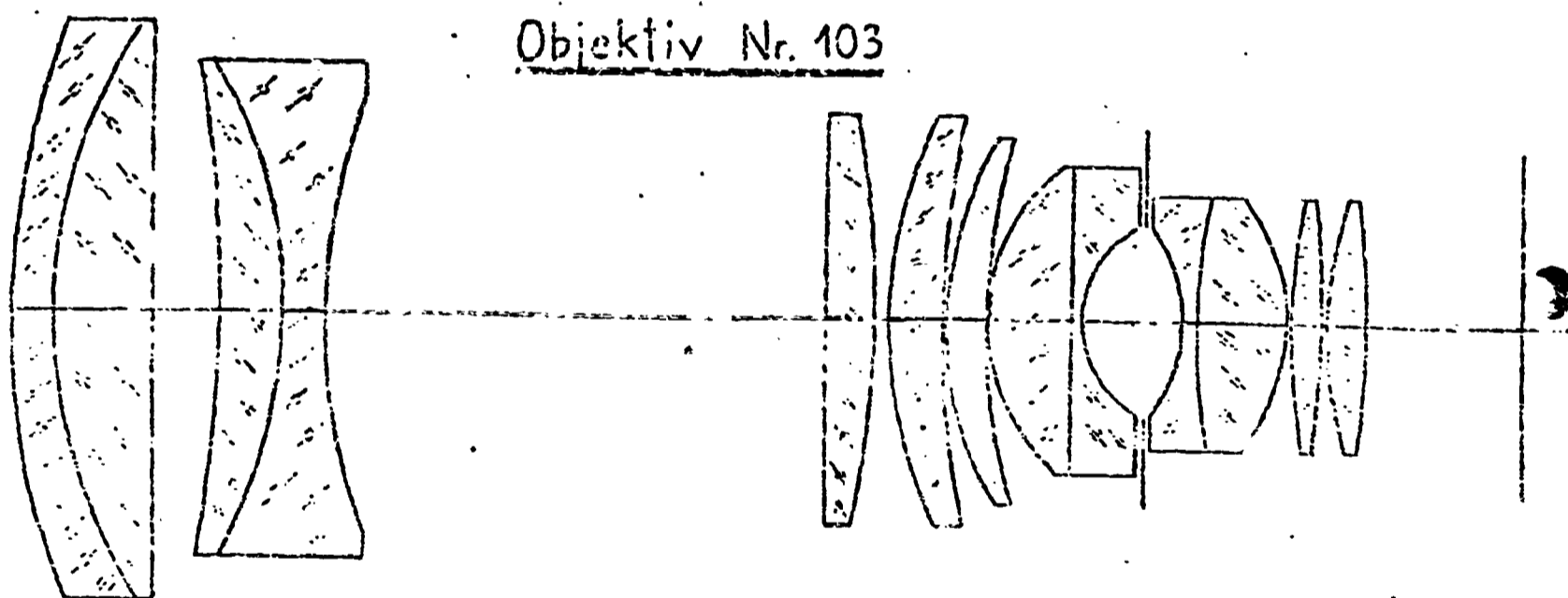


TABLE II-1

INDEX VALUES FOR BaF7 AND A DESIRE. VARIATION VAR 5

	Index BaF7	Index VAR 5	Δ Index BaF7 - VAR 5 $\times 10^5$
1	2	3	4
360	1,6439109	1,6482441	-433
380	1,6374185	1,6337929	-137
400	1,6321024	1,6322460	-14
420	1,6276770	1,6274335	24
440	1,6239420	1,6235928	25
460	1,6207526	1,6206403	11
480	1,6180015	1,6180494	-5
500	1,6156075	1,6157811	-17
520	1,6135076	1,6137490	-24
540	1,6116526	1,6118966	-24
560	1,6100033	1,6101853	-18
580	1,6085281	1,6083864	-6
600	1,6072014	1,6070863	11
620	1,6066020	1,6056639	34
640	1,6049126	1,6043096	60
660	1,6039184	1,6030137	90
680	1,6030072	1,6017683	124
700	1,6021687	1,6005665	160
720	1,6013941	1,5994029	199
740	1,6006757	1,5982724	240
760	1,6000071	1,5971703	284

TABLE II-2

INDEX VALUES FOR BaK5 AND A DESIRED VARIATION VAR 11

	Index BaK5	Index VAR 11	Index BaK5 - VAR 11 $\times 10^5$
1	2	3	4
λ_{nm}			
360	1,5812819	1,5850847	-380
380	1,5770658	1,5795119	-245
400	1,5735388	1,5751255	-159
420	1,5705518	1,5715831	-103
440	1,5679952	1,5686622	-67
460	1,5657861	1,5662120	-43
480	1,5638613	1,5641271	-27
500	1,5621713	1,5623312	-16
520	1,5606773	1,5607679	-9
540	1,5593479	1,5593944	-5
560	1,5581581	1,5581774	-2
580	1,5570872	1,5570909	0
600	1,5561185	1,5561143	0
620	1,5552377	1,5552307	1
640	1,5544332	1,5564264	1
660	1,5536952	1,5536902	1
680	1,5530153	1,5530125	0
700	1,5523863	1,5523857	0
720	1,5518022	1,5518031	0
740	1,5512578	1,5512590	0
760	1,5507485	1,5507485	0

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GLOSSARY

1. Refractive Index, n_i

The refractive index of a material may be defined as the ratio of light velocity in a vacuum to the light velocity in the material, and is commonly denoted by the letter n . Since the refractive index is a function of wavelength, its denotation commonly includes a subscript i which designates the associated wavelength. Often this subscript is a letter which represents a spectrum line of known wavelength and thus specifies the wavelength only in an indirect sense. Some subscripts commonly used in this manner are listed below:

g	$\lambda = 435.84 \text{ nm}$
F ¹	$\lambda = 479.94 \text{ nm}$
F	$\lambda = 486.13 \text{ nm}$
e	$\lambda = 546.07 \text{ nm}$
d	$\lambda = 587.56 \text{ nm}$
D	$\lambda = 589.29 \text{ nm}$
C ¹	$\lambda = 643.85 \text{ nm}$
C	$\lambda = 656.27 \text{ nm}$

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2. Dispersion

The variation in index with wavelength is called dispersion. It is often denoted as $\Delta n = n_{\lambda_1} - n_{\lambda_2}$ where λ_1 and λ_2 are the wavelengths for which the dispersion is given.

3. Relative Dispersion

Relative partial dispersion expresses the "spread" of two wavelengths of light as a fraction of the amount that light of a median wavelength m is bent. It is determined from the quantity $\Delta n / (n_m - 1)$.

4. Reciprocal Relative Dispersion, Abbe Value

Reciprocal Relative Dispersion represents the inverse of Relative Dispersion and is denoted by the symbol ν . When $\Delta n = n_F - n_C$ and $n_m = n_d$ it is commonly called a material's Abbe Value, ν_d .

5. Relative Partial Dispersion

The relative partial dispersion for the wavelengths x and y is commonly given by the equation

$$P_{x,y} = (n_x - n_y) / (n_F - n_C)$$

6. P^* , P^{**}

P^* is defined as the $P_{F,y}$ relative partial dispersion where y represents a wavelength of 1.01μ . P^{**} is defined as the $P_{F,y}$ relative partial dispersion where y represents a wavelength of $.365\mu$.

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7. Meridional Planes

The plane through an optical system containing the optical axis and the object point is termed the meridional plane for that object point. This plane is indicated in Figure G-1 by cross hatching from "northeast" to "southwest". Rays in this plane are referred to as meridional rays.

8. Sagittal Planes

A plane through the object point and perpendicular to the meridional plane is called the sagittal plane. It is indicated in Figure G-1 by cross hatching from "northwest" to "southeast". Rays in this plane are referred to as sagittal rays.

9. Numerical Aperture, N.A.

The numerical aperture of a system is defined as the product of the value of the refractive index of the medium in which the image lies times the sine of the half angle of the cone of illumination. It is commonly denoted by the abbreviation, N.A.

10. Optical System Aberrations

A system is said to exhibit aberrations if, after passing through the system, rays originating from a point in the object are not recombined at a point in the image.

MERIDIONAL AND SAGITTAL PLANES
FOR OBJECT POINT P

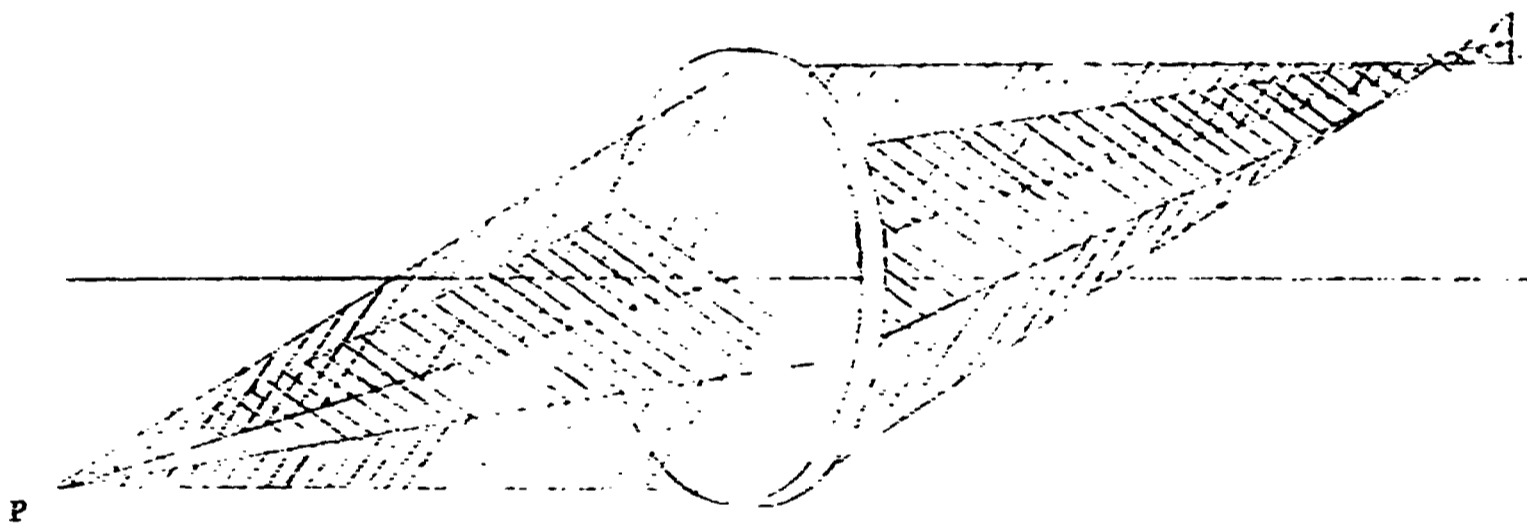


FIGURE G-1

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11. Longitudinal Chromatic Aberration

Longitudinal Chromatic Aberration refers to the variation of focus (or image position) with wavelength.

12. Lateral Chromatic Aberration

Lateral Chromatic Aberration refers to the variation of magnification with wavelength.

13. Achromatization

Achromatization refers to the correction of the Chromatic Aberration of a system at two wavelengths.

14. Secondary Spectrum

Secondary Spectrum refers to the residual chromatic aberration exhibited by an achromatic system at wavelengths other than those for which the correction was evaluated.

15. Apochromat

An apochromat refers to a system which is corrected for Chromatic Aberration at three wavelengths.

16. Spherical Aberration

Spherical Aberration is defined as the variation of focus with aperture. Rays passing through the system close to the optical

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axis are imaged at a different point than those which pass through the system at a greater distance from the optical axis.

17. Zonal Spherical Aberration

Zonal Spherical Aberration refers to the residual spherical aberration exhibited by a system which has been corrected for spherical aberration at selected zones.

18. Spherochromatism

Spherochromatism refers to the variation of spherical aberration with wavelength.

19. Coma

Coma refers to an optical aberration which may be described as a variation of magnification with aperture. Rays passing through the margin of a lens exhibit a different magnification than central rays.

20. Aspheric Surface

An aspheric surface represents a nonspherical surface which exhibits rotational symmetry about the lens axis. To the designer, each term in the polynomial, which describes the departure of an asphere from the closest fitting sphere, is an additional degree of freedom available for the correction of aberrations. Conic sections such as parabolas, ellipses, and hyperbolas are commonly used.

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21. Γ , GAMMA

Γ is a figure of merit which describes the expected optical path variations which would be introduced by a refractive material which was subjected to temperature changes. For a material of refractive index, n , and thermal expansion coefficient, α , it may be computed from the relation

$$\Gamma = dn/dt + \alpha(n-1)$$

22. Catadioptric System

A catadioptric optical system is one which utilizes both reflective (mirror) and refractive (lens) components.

23. Fresnel Losses

Fresnel Losses refer to the decrease in transmitted energy of a system due to reflections at boundaries. For light normally incident on the boundary which separates two media of indices n and n^1 respectively, the fraction of incident light which is refracted is given by the following relation:

$$R = (n^1 - n)^2 / (n^1 + n)^2$$

24. X.U.V.

X.U.V. is an abbreviation used to denote the Extreme Ultraviolet region of the Electromagnetic Spectrum which is generally taken as extending below 600\AA .

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25. V.U.V.

V.U.V. is an abbreviation used to denote the vacuum ultraviolet region of the Electromagnetic Spectrum which is generally taken as extending from 1650Å to the X.U.V.

26. IRG

IRG is a code name prefix used to designate several infrared transmitting materials currently manufactured by Schott.

27. AR

AR is an abbreviation used to denote antireflection coatings. They are commonly used to reduce fresnel losses at lens surfaces.

28. C.R.T.

C.R.T. is an abbreviation used to denote a cathode ray tube. These are commonly used to convert electrical signals to optical displays.

APPENDIX II

INDUCTION MELTING POWER REQUIREMENT CALCULATIONS

By making certain assumptions and by deeming some factors as insignificant, the power requirements to induction heat 0.5 inch diameter spheres of four materials (90% Ta_2O_5 - 10% CaO; 85% Nb_2O_5 - 15% CaO; 80% Al_2O_3 - 20% SiO_2 ; and 100% La_2O_3) to 200 C above their melting point, from a preheat temperature of 2000F, can be calculated. Table II-1 lists the assumptions and gives the results of these calculations both with and without the use of a reflector. Table II-2 shows a sample calculation for one material and the equations used to arrive at the results. The power requirements for the preheating to 2000F are not included in these results, but can be considered to be small in comparison to that required, largely to overcome radiation losses, at the higher temperatures. The calculations must be recognized as approximations for the following reasons:

- (1) Heat loss by conduction and convection are not included. This loss is dependent upon the thermal conductivity of the atmosphere, velocity of the atmosphere, and a relative size factor. However, these losses may be considered trivial.
- (2) The exact melting point and emissivity at elevated temperatures has not been measured and are given as best estimates.
- (3) The emissivity and specific heat are not constant over the temperature range of interest.
- (4) The values for specimen size, the efficiency of the reflector, the total time to heat, the surrounding temperature, the coil efficiency and the power supply efficiency, are assumed values based on reasonable conditions.

It is difficult to estimate an error of calculations for these results. One might take the "worst" condition for each of the variables and recalculate the power

requirements. Realistically, however, it is not probable that all variables will reach this extreme. Some variables may even have more favorable values and some can be controlled in the experiment. What the results do show, as they are presented, is the magnitude of the power requirements for induction heating of these candidate materials; that they are not inconceivable for an experiment of this type and are as a matter of fact, well within reasonable expectations; and what factors do effect the requirements and should be investigated further if greater accuracy of the calculations is required.

Table II-1 Calculated Power Requirements to Induction Heat 0.5-Inch Spheres
of Four Materials to 200C above their Melting Point

Conditions	Material			
	90 w/o Ta ₂ O ₅ - 10 w/o CaO	85 w/o Nb ₂ O ₅ - 15 w/o CaO	80 w/o Al ₂ O ₃ - 20 w/o SiO ₂	100 w/o La ₂ O ₃
Approximate Melting point (°C)	1875	1540	1920	2210
Superheat Temperature (°C)	2075	1740	2120	2410
Density (lbs/ft ³)	545	278	220	409
Specific heat (of pure oxide) (BTU/lb°F)	0.11	0.17	0.3	.11
Heat of fusion (BTU/lb.)	131.1	92.5	82.6	128.0
Heat of transformation	No trans.	No trans.	No trans.	No trans.
Est. Emissivity at MP	.5	.5	.5	.5
Total time to heat (hr)	.25	.25	.25	.25
Surrounding temp (°K)	500	500	500	500
Coil efficiency (assumed)	.2	.2	.2	.2
Power supply efficiency (assumed)	.6	.6	.6	.6
<u>Calculations</u>				
t _f (hr)	.10	.08	.03	.08
t _c (hr)	.18	.17	.22	.17
P ₁ (watts)	15.8	7.2	12.8	14.2
P ₂ (watts)	436	235	473	745
P ₃ (watts)	1808	970	1943	3038
P _T (100%)	2260	1212	2429	3797
<u>Results (Including power supply eff)</u>				
P _T (without reflector) (KW)	3.8	2.0	4.0	6.3
P _T (with reflector of 85% eff) (KW)	1.1	.6	1.1	1.7

NOTES: (1) Heat loss by conduction & convection are not included because it should be significant for these high temperature materials.

(2) The calculations are for induction heating only, from the preheat temperature 2000F to 200C above the melting point. Preheat power requirements are not included.

Table II-2 Sample Calculation for Induction Melting of
80 w/o Al_2O_3 - 20 w/o SiO_2

Basic Assumptions

1. Size: 0.50 inch diameter
2. Melting point: $1920^{\circ}C$ ($3488^{\circ}F$)
3. Max. Temp.: $2120^{\circ}C$ ($3848^{\circ}F$) [T_2] $2393^{\circ}K$
4. Preheat Temp.: $2000^{\circ}F$
5. Specific heat: 0.3 BTU/lb $^{\circ}F$ (of pure oxide) [C]
6. Heat of fusion: 45.9 cal/gram (83.6 BTU/lb)
7. Thermal emissivity (est.): 0.5 [E]
8. Density: 3.54 gm/cc (220 lb/ft^3) $M = 0.0083 \text{ lbs.}$
9. Total time to heat: .25 hr [t_T]
10. Surrounding temp.: 500 K [T_1]
11. Coil efficiency: 0.2

Other Definitions

M = mass, lbs

T = temperature rise, $^{\circ}F$

H_f = heat of fusion, BTU/lb.

t_c = time to achieve temperature rise, hr.

t_f = time to expend heat of fusion, hr.

t_T = total time to heat, hr.

E_e = effective emissivity

ϵ_1 = emissivity of the melt

ϵ_2 = emissivity of a spherical, specular reflector surrounding the spherical melt

P_1 = Req. power to be supplied to the load = $\frac{M}{3.412} \left(\frac{TC}{t_c} + \frac{H_f}{t_f} \right)$, watts

P_2 = radiated power loss = $5.7AE \left[\left(\frac{T_2}{1000} \right)^4 - \left(\frac{T_1}{1000} \right)^4 \right]$, watts

Other Definitions (Cont'd)

$$P_3 = \text{Power loss in the coil} = (P_1 + P_2) \left(\frac{1}{\text{eff}} - 1 \right), \text{ watts}$$

$$P_T = \text{Total power} = P_1 + P_2 + P_3, \text{ watts}$$

$$A = \text{Surface area of the work, cm}^2$$

Assume that heat input is done at a constant rate of BTU's so that total time (t_T) consists of a ratio of:

$$t_T = t_c + t_f \text{ where } t_f = t_T \left(\frac{H_f}{TC + H_f} \right)$$

$$t_c = t_T \left(\frac{TC}{TC + H_f} \right)$$

Calculations

$$\text{I. } t_T = t_c + t_f \quad \text{or } t_c = t_T - t_f$$

$$t_f = t_T \left(\frac{H_f}{TC + H_f} \right)$$

$$t_f = .25 \left[\frac{82.6}{(3848 - 2000) .3 + 82.6} \right]$$

$$t_f = .25 (.128) = .032 \text{ hr.}$$

$$t_c = .25 - .03 = .22 \text{ hr.}$$

$$P_1 = \frac{M}{3.412} \left(\frac{TC}{t_c} + \frac{H_f}{t_f} \right)$$
$$= \frac{0.0083}{3.412} \left(\frac{1848 \times .3}{.22} + \frac{82.6}{.03} \right)$$

$$= 12.8 \text{ watts}$$

$$P_2 = 5.7 \text{ AE} \left[\left(\frac{T_2}{1000} \right)^4 - \left(\frac{T_1}{1000} \right)^4 \right]$$
$$= 5.7 \times 5.06 \times .5 \left[\left(\frac{2393}{1000} \right)^4 - \left(\frac{500}{1000} \right)^4 \right]$$

$$= 473.0 \text{ watts}$$

Calculations (Cont'd)

$$\begin{aligned}P_3 &= (P_1 + P_2) \left(\frac{1}{\text{eff}} - 1 \right) \\&= (13 + 473.0) \left(\frac{1}{0.2} - 1 \right) \\&= 1943 \text{ watts}\end{aligned}$$

$$\begin{aligned}P_T &= P_1 + P_2 + P_3 \\&= 13 + 473 + 1943 \\&= 2429 \text{ watts} = 2.4 \text{ KW}\end{aligned}$$

II Assume 0.6 induction unit efficiency

$$P_T = \frac{2.4}{0.6} = 4 \text{ KW}$$

III Assume spherical reflector where 85% of radiated power is reflected back into melt

$$P_1 = 13 \text{ watts (from above)}$$

$$P_2 = 5.7 \text{ AE} \left[\left(\frac{T_2}{1000} \right)^4 - \left(\frac{T_1}{1000} \right)^4 \right]$$

$$\text{where } E = \frac{1}{1/\epsilon_1 + 1/\epsilon_2 - 1}$$

ϵ_1 = Emissivity of melt

ϵ_2 = Emissivity of reflector

$$E = \frac{1}{1/.5 + 1/.15 - 1} = .13$$

$$= 5.7 \times 5.06 \times .13 \left[\left(\frac{2393}{1000} \right)^4 - \left(\frac{500}{1000} \right)^4 \right] = 123 \text{ watts}$$

$$\begin{aligned}P_3 &= (P_1 + P_2) \left(\frac{1}{\text{eff}} - 1 \right) \\&= 13 + 123 \left(\frac{1}{0.2} - 1 \right) = 544 \text{ watts}\end{aligned}$$

$$\begin{aligned}P_T &= P_1 + P_2 + P_3 \\&= 13 + 123 + 544 = 680 \text{ watts}\end{aligned}$$

and at .6 power efficiency

$$\frac{680}{0.6} = 1133 \text{ watts or 1.1 kilowatts}$$